# Macrocyclic Stereocontrol in Organic Synthesis: I. Efforts toward the Synthesis of (-)-Tetracycline II. Analysis of the Peripheral Attack Model

# *Abstract*

**Macrocyclic Stereocontrol in Organic Synthesis:**

**I. Efforts Toward the Synthesis of (–)-Tetracycline**

**II. Analysis of the Peripheral Attack Model**

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*Professor David A. Evans* *August 2012*

**I. Efforts Toward the Synthesis of (–)-Tetracycline**

A macrocyclic approach toward (–)-tetracycline is described. Traditional approaches towards the synthesis of tetracycline antibiotics employ the linear construction of the core structure starting with either the A- or D-rings. In contrast to this iterative annulation-based strategy, we have sought to employ a chiral macrocycle in our approach. Key to the success of our synthesis endeavor is the execution of two key steps: (1) a transannular Michael addition, which forms the A-ring and sets the C4a-stereogenic center; and (2) an isoxazole substitution reaction, which effects a ring contraction to produce both the B- and C-rings. This work describes our implementation of the strategy and focuses on the stereochemical interplay between the C4-, C4a-, C6-, and C12a-stereocenters within the context of the key steps.

**II. Analysis of the Peripheral Attack Model**

The application of the peripheral attack model to 34 literature examples of intermolecular macrocyclic stereocontrol is described. While the peripheral attack model has been broadly applied in complex molecule synthesis, the validity of the model has not been subjected to analysis since being proposed in the early 1980's. In order to assess the

value of the model to organic chemists, we have developed a systematic method for probing the conformational profile of macrocycles. Using this tool, we then analyzed each of the 34 literature substrates and concluded whether the peripheral attack model predicts the correct stereochemical outcome in both a binary- and magnitude-based capacity. Analysis of both the bulk dataset and subsets of the dataset is included.

## *Acknowledgments*

I would like to acknowledge my advisor, Professor David Evans, for his significant contributions to my development as both a scientist and person. Dave has an unparalleled passion for organic chemistry, which captivates and energizes those who train under his guidance. This passion, coupled with his aptitude for education translated wonderfully to my graduate school experience as I sought to learn how to approach and solve scientific problems. An incredibly valuable characteristic of this education within the "Evans School" was that Dave offered far more suggestions than directives, meaning that I was responsible for critical decisions within the project. There is no better way to learn, and I know this experience will be invaluable as I seek solutions to problems in the future. Thank you for everything Dave.

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nificantly, Laura Brozek. Thank you for the love, support, and advice that were provided during critical times in graduate school. I anxiously await all of the wonderful places that life takes us.

# *Table of Contents*

## *Chapter 1: Introduction*



## *Chapter 2: Synthesis of the First Generation Macrocycle*

## *Chapter 3: Synthesis of the Second Generation Macrocycle*

## *Chapter 4: Execution of a Transannular Cascade*



## *Chapter 5: Analysis of the Peripheral Attack Model*

# *List of Abbreviations*

| | |
|---|---|
| AB | AB spin system (Pople notation) |
| ap. | apparent |
| aq. | aqueous |
| Ar | aromatic (generic) |
| atm | atmosphere |
| Bn | benzyl |
| Boc | *tert*-butoxycarbonyl |
| $Boc_2O$ | di-*tert*-butyldicarbonate |
| br. s | broad singlet |
| brsm | based on recovered starting material |
| Bu | butyl |
| *c* | concentration (g/100 mL) |
| COSY | correlation spectroscopy |
| CSA | camphorsulfonic acid |
| *d* | deutero |
| d | doublet |
| DCE | 1,2-dichloroethane |
| DIBAl-H | di-*iso*-butylaluminum hydride |

| | |
|---|---|
| DIPEA | di-*iso*-propylethylamine (Hünig's base) |
| DME | dimethoxyethane |
| DMF | dimethylformamide |
| DMP | Dess-Martin periodinane |
| DMS | dimethylsulfide |
| DMSO | dimethylsulfoxide |
| dr | diastereomeric ratio |
| *E* | entgegen |
| *ee* | enantiomeric excess |
| ESI | electrospray ionization |
| Et | ethyl |
| g | gram(s) |
| h | hour(s) |
| HMDS | hexamethyldisilazane |
| HMBC | heteronuclear multiple bond correlation |
| HPLC | high performance liquid chromatography |
| HRMS | high resolution mass spectrometry |
| HSQC | heteronuclear single quantum coherence |
| Hz | hertz |

| | |
|---|---|
| Im | imidazole |
| IR | infrared spectroscopy |
| *J* | coupling constant |
| KHMDS | potassium hexamethyldisilazide |
| LDA | lithium diisopropylamide |
| LiHMDS | lithium hexamethyldisilazide |
| Lut | 2,6 lutidine |
| *m* | meta |
| m | multiplet |
| M | molar (moles/liter) |
| *m/z* | mass to charge ratio |
| m-CPBA | *meta*-chloroperoxybenzoic acid |
| Me | methyl |
| min | minute(s) |
| mL | milliliter(s) |
| mol | mole(s) |
| MOM | methoxymethyl |
| MS | mass spectrometry |
| Ms | methanesulfonyl |

| | |
|---|---|
| NCS | N-chlorosuccinimide |
| NMO | N-methylmorpholine-N-oxide |
| NMR | nuclear magnetic resonance |
| nOe | nuclear Overhauser effect |
| *o* | ortho |
| ºC | degrees Celsius |
| OTf | trifluoromethanesulfonyl |
| *p* | para |
| Ph | phenyl |
| ppm | parts per million |
| PPTS | pyridinium *para*-toluenesulfonate |
| pyr | pyridine |
| *R* | rectus (Cahn-Ingold- Prelog system) |
| R | alkyl group (generic) |
| RCM | ring-closing metathesis |
| $R_f$ | retention factor |
| rt | room temperature |
| *S* | sinister (Cahn-Ingold-Prelog system) |
| s | singlet |

| | |
|---|---|
| t | triplet |
| *t* | tertiary |
| TBAF | tetra(*n*-butyl)ammonium fluoride |
| TBAI | tetra(*n*-butyl)ammonium iodide |
| TBDPS | *tert*-butyldiphenylsilyl |
| TBS | *tert*-butyldimethylsilyl |
| TES | triethylsilyl |
| TFA | trifluoroacetic acid |
| THF | tetrahydrofuran |
| TLC | thin layer chromatography |
| TMS | tetramethylsilyl |
| Ts | *para*-toluenesulfonyl |
| *vic.* | vicinal |
| q | quartet |
| quant. | quantitative |
| *Z* | zusammen |
| δ | chemical shift (parts per million) |

# *Chapter 1*

## Introduction

### I. Discovery of the First Tetracyclines

In 1948, Benjamin M. Duggar, a researcher for American Cyanamid Company reported the discovery of a new organism, *Streptomyces aureofaciens*, from a timothy field in Missouri.[1] The name *aureofaciens* was used to describe both the golden yellow pigment found in the mycelium, and the golden yellow color of an antibiotic isolated from this organism. The antibiotic, appropriately named aureomycin (chlorotetracycline, **1.1**, Figure 1.1), showed broad-spectrum antibiotic activity toward both Gram-positive and Gram-negative organisms, as described by associated *in vitro*,[2] *in vivo*,[3] and preliminary clinical trial[4] data that followed the initial isolation report. A subsequent disclosure by researchers at Chas. Pfizer and Co. in 1950 revealed the isolation of another antibiotic, terramycin (oxytetracycline, **1.2**, Figure 1.1), from a new actinomycete *Streptomyces ri-*

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[1] (a) Duggar, B. M. *Ann. N. Y. Acad. Sci.* **1948**, *51*, 177-181. (b) Duggar, B. M. Aureomycin and Preparation of the Same. U.S. Patent 2,482,055, Sept. 13, 1949.

[2] (a) Price, C. W.; Randall, W. A.; Welch, H. *Ann. N. Y. Acad. Sci.* **1948**, *51*, 211-217. (b) Chandler, C. A.; Bliss, E. *Ann. N. Y. Acad. Sci.* **1948**, *51*, 221-227.

[3] (a) Little, P. A. *Ann. N. Y. Acad. Sci.* **1948**, *51*, 246-253. (b) Bryer, M. S.; Schoenbach, E. B.; Bliss, E. A.; Chandler, C. A. *Ann. N. Y. Acad. Sci.* **1948**, *51*, 254-266.

*mosus*.[5] Together, these natural products captured the attention of the scientific community of the time, as researchers realized the importance of novel antibiotics in the face of emerging β-lactam resistance.[6]

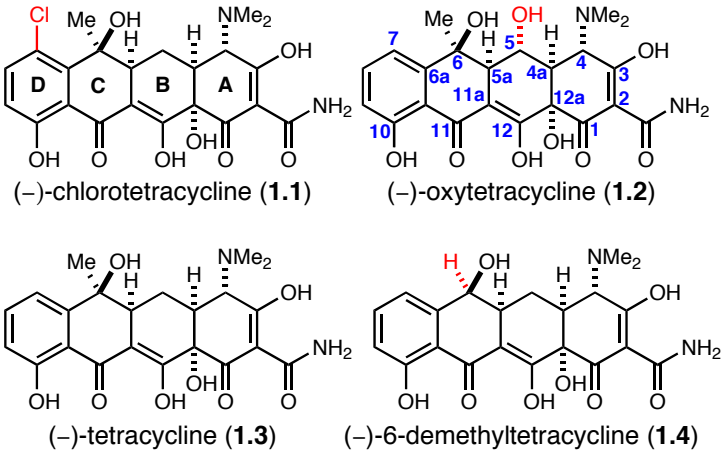


**Figure 1.1** Naturally occurring tetracycline antibiotics.

Lacking significant structural information, researchers were unaware of the architectural homology between terramycin and aureomycin upon discovery. Yet, *in vitro* evaluation of terramycin revealed a similarly broad-spectrum of activity to that of aureomycin, a relationship that was documented in the initial isolation report.[5] The gross structure of these two compounds was later elucidated through the efforts of R. B. Woodward in collaboration with researchers from Pfizer.[7] However, the absolute[8] and relative[9] stereochemistry was not established until years later.

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[4] (a) Collins, H. S.; Paine, T. F. Jr.; Finland, M. *Ann. N. Y. Acad. Sci.* **1948**, *51*, 231-240. (b) Schoenbach, E. B.; Bryer, M. S.; Long, P. H. *Ann. N. Y. Acad. Sci.* **1948**, *51*, 267-279.

[5] Finlay, A. C.; Hobby, G. L.; P'an, S. Y.; Regna, P. P.; Routien, J. B.; Seeley, D. B.; Shull, G. M.; Sobin, B. A.; Solomons, I. A.; Vinson, J. W.; Kane, J. H. *Science* **1950**, *111*, 85.

[6] (a) Medeiros, A. A. *Clin. Infect. Dis.* **1997**, *24(suppl. 1)*, S19-45. (b) Chambers, H. F. *Emerg. Infect. Dis.* **2001**, *7*, 178-182. (c) Wenzel, R. P. *N. Engl. J. Med.* **2004**, *351*, 523-526.

[7] (a) Hochstein, F. A.; Stephens, C. R.; Conover, L. H.; Regna, P. P.; Pasternack, R.; Brunings, K. J.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 3708-3709. (b) Stephens, C. R.; Conover, L. H.; Hochstein, F. A.;

Tetracycline (**1.3**) was introduced initially to the scientific literature in 1953 as a hydrogenation product of aureomycin (Figure 1.1).[10] However, in 1956 tetracycline was also determined to be a naturally occurring substance, having been isolated from the fermentation broth of *Streptomyces aureofaciens* acquired from a Texas soil sample.[11] In the following year, 6-demethyltetracycline (**1.4**), now a fourth naturally occurring tetracycline, was discovered from a mutant strain of the original *Streptomyces aureofaciens* organism isolated by Duggar.[12] This latter discovery capped an amazing decade of tetracycline antibiotic discovery.

**II. Discovery of Additional Tetracycline Natural Products**

More recently, additional tetracyclines have been discovered, expanding the structural complexity and known bioactivity of this natural product class (Figure 1.2).[13] Dactylocycline A (**1.5**) and B (**1.6**), isolated via fermentation of *Dactylosporangium* sp.

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F. A.; Regna, P. P.; Pilgrim, F. J.; Brunings, K. J.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 4976-4977. (c) Hochstein, F. A.; Stephens, C. R.; Conover, L. H.; Regna, P. P.; Pasternack, R.; Gordon, P.N.; Pilgrim, F. J.; Brunings, K. J.; Woodward, R. B. *J. Am. Chem. Soc.* **1953**, *75*, 5455-5475. (d) Stephens, C. R.; Conover, L. H.; Pasternack, R.; Hochstein, F. A.; Moreland, W. T.; Regna, P. P.; Pilgrim, F. J.; Brunings, K. H.; Woodward, R. B. *J. Am. Chem. Soc.* **1954**, *76*, 3568-3575.

[8] Dobrynin, V. N.; Gurevich, A. I.; Karapetyan, M. G. *Tet. Lett.* **1962**, *20*, 901-904.

[9] (a) Hirokawa, S.; Okaya, Y.; Lovell, F. M.; Pepinski, R. *Acta. Crys.* **1959**, *12*, 811-812. (b) Hirokawa, S.; Okaya, Y.; Lovell, F. M.; Pepinsky, R. *Z. Krys.* **1959**, *112*, 439-464. (c) Takeuchi, Y.; Buerger, M. J. *PNAS* **1960**, *46*, 1366-1370. (d) Donohue, J.; Dunitz, J. D.; Trueblood, K. N.; Webster, M. S. *J. Am. Chem. Soc.* **1963**, *85*, 851-856. (e) von Wittenau, M. S.; Blackwood, R. K.; Conover, L. H.; Glauert, R. H.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 134-135.

[10] (a) Booth, J. H.; Morton II, J.; Petisi, J. P.; Wilkinson, R. G.; Williams, J. H. *J. Am. Chem. Soc.* **1953**, *75*, 4621. (b) Conover, L. H.; Moreland, W. T.; English, A. R.; Stephens, C. R.; Pilgrim, F. J. *J. Am. Chem. Soc.* **1953**, *75*, 4622-4623.

[11] Minieri, P. P.; Sokol, H.; Firman, M. C. U. S. Patent 2,734, 018, Feb 7, 1956.

[12] (a) McCormick, J. R. D.; Sjolander, N. O.; Hirsch, U.; Jensen, E. R.; Doerschuk, A. P. *J. Am. Chem. Soc.* **1957**, *79*, 4561-4563. (b) Webb, J. S.; Broschard, R. W.; Cosulich, D. B.; Stein, W. J.; Wolf, C. F. *J. Am. Chem. Soc.* **1957**, *79*, 4563-4564. (c) Boothe, J. H.; Green, A.; Petisi, J. P.; Wilkinson, R. G.; Waller, C. W. *J. Am. Chem. Soc.* **1957**, *79*, 4564.

[13] Pickens, L. B.; Kim, W.; Wang, P.; Zhou, H.; Watanabe, K.; Gomi, S.; Tang, Y. *J. Am. Chem. Soc.* **2009**, *131*, 17677-17689.

SC14051 (ATCC 53693), display activity toward tetracycline resistant strains of *S. aureus* and *S. epidermidis*.[14] Further, novel C-glycosylated tetracyclines SF2575 (TAN-1518X, **1.7**),[15] TAN-1518A (**1.8**),[16] and TAN-1518B (**1.9**), have demonstrated intriguing anti-tumor activities via inhibition of DNA topoisomerase I. Collectively, these more recently discovered tetracyclines further validate the relevance of the core structure as a privileged template for molecular recognition within biological systems.

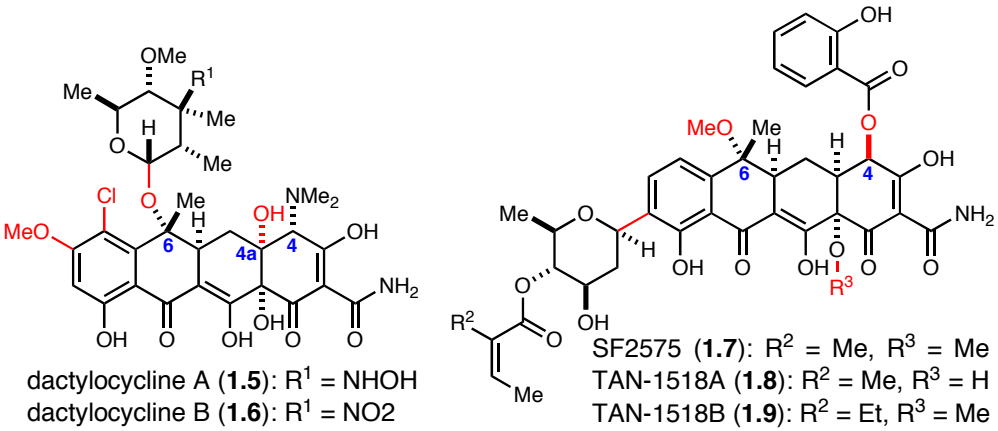


**Figure 1.2** Structure of several tetracycline antibiotics that have been discovered more recently.

Of particular intrigue is the perturbation of previously conserved stereochemical relationships within the classic tetracyclines when compared to those in Figure 1.2. For example, the C4 substituent within SF2575 and TAN-1518A- and B is now beta, which

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[14] (a) Wells, J. S.; O'Sullivan, J.; Aklonis, C.; Ax, H. A.; Tymiak, A. A.; Kirsch, D. R.; Trejo, W. H.; Principe, P. *J. Antibiot.* **1992**, *45*, 1892-1898. (b) Tymiak, A. A.; Ax, H. A.; Bolgar, M. S.; Kahle, A. D.; *J. Antibiot.* **1992**, *45*, 1899-1906. (c) Devasthale, P. V.; Mitscher, L. A.; Telikepalli, H.; Velde, D. V.; Zou, J.-Y.; Ax, H. A.; Tymiak, A. A. *J. Antibiot.* **1992**, *45*, 1907-1913.

[15] Hatsu, M.; Sasaki, T.; Watabe, H.; Miyadoh, S.; Nagasawa, M.; Shomura, T.; Sezaki, M.; Inouye, S.; Kondo, S. *J. Antibiot.* **1992**, *45*, 320-324. (b) Hatsu, M.; Sasaki, T.; Gomi, S.; Kodama, Y.; Sezaki, M.; Inouye, S.; Kondo, S. *J. Antibiot.* **1992**, *45*, 325-330.

[16] Horiguchi, T.; Hayashi, K.; Tsubotani, S.; Iineuma, S.; Harada, S.; Tanida, S. *J. Antibiot.* **1994**, *47*, 545-556.

places the group within the concave face of the *cis*-decalin subunit of the A- and B-rings. Further, The C6-stereogenic center is now inverted with respect to tetracycline, placing the methoxide substituent *alpha*. It is intriguing to consider the implications of these resident stereocenters in the context of a larger synthesis effort.

**III. Structure and Reactivity of Tetracycline**

Structurally, tetracycline is a densely functionalized type II polyketide containing multiple sites of oxidation in addition to dimethylamine and vinyligous carbamic acid functions. In large part, the polar functionalities exist in the southern region of the molecule (C10-C2) in the form of an aryl hydroxyl in the D-ring, a 1,3-diketone moiety bridging the C- and B-rings, and a tertiary carbinol at C12a. The northern region of tetracycline is rich in stereogenic centers (C4-C6), containing a tertiary carbinol at C6, two tertiary carbon centers at C5a and C4a, and a dimethyl amino group at C4. Yet, the feature that defines the three-dimensional architecture of tetracycline is the cis ring fusion that joins the C4a and C12a stereogenic centers. This ring fusion forces the molecule to depart from planarity, establishing a concave and convex face to the overall structure (Figure 1.3).[17]

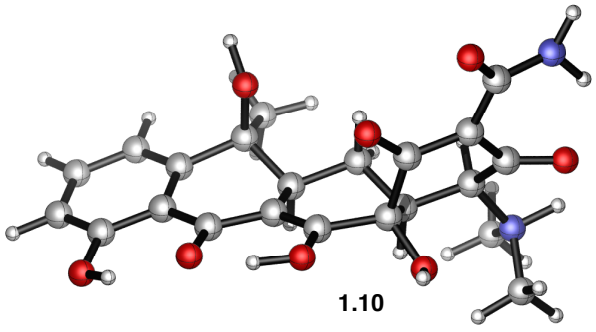


**Figure 1.3** X-ray crystal structure of tetracycline hexahydrate (water molecules omitted for clarity).[17]

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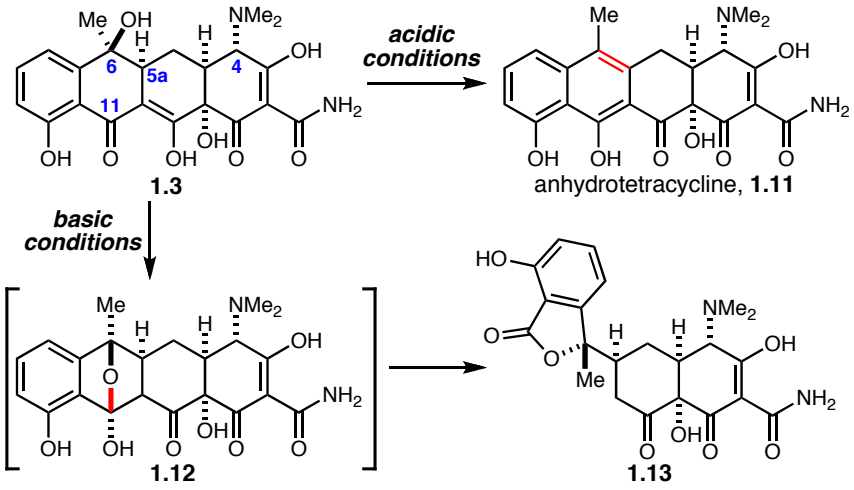
[17] Caira, M. R.; Nassimbeni, L. R.; Russell, J. C. *Acta Crys*. **1977**, *B33*, 1171-1176.

The extensive oxidation of the carbocyclic framework within the tetracycline core structure results in an intriguing reactivity profile that is largely dominated by the C6-tertiary carbinol.[7d] Specifically, in the presence of acidic conditions the C6-tertiary carbinol may be protonated, facilitating the elimination of this function and aromatization of the C-ring to produce anhydrotetracycline (**1.11**, Scheme 1.1). Alternatively, under basic conditions, fragmentation of the B-ring may occur to produce **1.13** through the intermediacy of hemi-acetal **1.12**. The C4-stereocenter is also sensitive to pH, as it is possible to epimerize the C4-dimethylamine moiety via exposure of tetracycline to slightly acidic conditions (pH 4.6), which produces a 1.5:1 mixture of tetracycline : 4-epi-tetracycline.[18]

**Scheme 1.1** Decomposition pathways relevant to the C6-tertiary carbinol.[7d]




[18] (a) Doerschuk, A. P.; Bitler, B. A.; McCormick, J. R. D. *J. Am. Chem. Soc.* **1955**, *77*, 4687. (b) Stephens, C. R.; Conover, L. H.; Gordon, P. N.; Pennington, F. C.; Wagner, R. L.; Brunings, K. J.; Pilgrim, F. J. *J. Am. Chem. Soc.* **1956**, *78*, 1515-1516. (c) McCormick, J. R. D.; Fox, S. M.; Smith, L. L.; Bitler, B. A.; Reichenthal, J.; Origoni, V. E.; Muller, W. H.; Winterbottom, R.; Doerschuk, A. P. *J. Am. Chem. Soc.* **1956**, *78*, 3547-3548.

## IV. The Bacterial Ribosome as a Target for Antibiotics

The tetracycline antibiotics are part of a larger group of natural products whose fundamental function is the disruption of protein biosynthesis in bacteria.[19] This mechanism of action involves binding to the bacterial ribosome, a complex machine tasked with the biosynthesis of proteins critical for cellular viability.[20] Structurally, the bacterial ribosome is comprised of two components, the 30S and 50S subunits which together produce the complete 70S ribosome (Figure 1.4).[21,22] Protein synthesis occurs via utilization of three tRNA binding sites that are present when the two subunit structure is intact, known as the A (aminoacyl), P (peptidyl), and E (exit) sites.

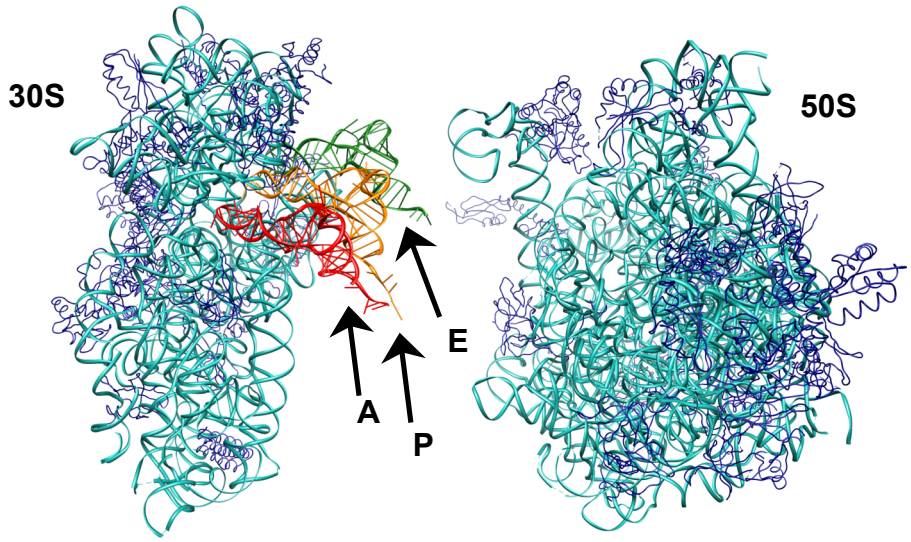



**Figure 1.4** Crystal structure of the ribosome from *Thermus thermophilus*.[22]

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[19] Poehlsgaard, J.; Douthwaite, S. *Nat. Rev. Microbiol.* **2005**, *3*, 870-881.

[20] (a) Ramakrishnan, V. *Cell* **2002**, *108*, 555-572. (b) Schmeing, T. M.; Ramakrishnan, V. *Nature* **2009**, *461*, 1234-1242.

[21] The unit S is an abbreviation for "Svedborg", which represents the rate of sedimentation in centrifugation; this unit is non-additive.

[22] Yusupov, M. M.; Yusupova, G. Z.; Baucom, A.; Lieberman, K.; Earnest, T. N.; Cate, J. H. D.; Noller, H. F. *Science* **2001**, *292*, 883-896.

Given that targets critical to viability are considered attractive targets for antibiotic intervention, it is not surprising that the ribosome is considered one of four fundamental targets for antibacterial agents.[23] Further, natural products have emerged that target multiple locations within the ribosome on either the 30S or 50S subunits. For example, well-known macrolide antibiotics such as erythromycin (**1.15**)[24] inhibit protein synthesis via blockage of the tunnel into which the growing peptide travels during protein synthesis. Erythromycin specifically targets the 50S subunit to carry out this task. Other natural products that target the 50S subunit, which include virginiamycin (**1.14**) and chloramphenicol (**1.16**, Figure 1.5), may bind to different regions within the subunit in order to inhibit protein synthesis at another juncture in the cycle.[25] Small molecules also target the 30S subunit of the bacterial ribosome. For example, the aminoglycoside antibiotics paromomycin (**1.17**) and geneticin (**1.18**) bind to the decoding region of the A-site, perturbing the conserved process of codon-anticodon recognition necessary for proper protein synthesis.[19] This perturbation results in the synthesis of proteins with errors in the overall amino acid sequence.

Biochemical[26] and crystallographic[27] evidence has revealed that tetracycline also targets the 30S subunit of the bacterial ribosome. The primary site of binding is found

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[23] *Antibiotics: Actions, Origins, Resistance;* Walsh, C. ASM Press: Washington, DC, 2003.

[24] Saltzman, L.; Apirion, D. *Molec. gen. Gen.***1976**, *143*, 301-306.

[25] (a) Parfait, R.; Cocito, C. *Proc. Natl. Acad. Sci.* **1980**, *77*, 5492-5496. (b) Long, K. S.; Porse, B. T. *Nuc. Acids Res*. **2003**, *31*, 7208-7215.

[26] Goldman, R. A.; Hasan, T.; Hall, C. C.; Strycharz, W. A.; Cooperman, B. S. *Biochemistry* **1983**, *22*, 359-368.

[27] (a) Broderson, D. E.; Clemons, Jr.; W. M.; Carter, A. P.; Morgan-Warren, R. J.; Wimberly, B. T.; Ramakrishnan, V. *Cell* **2000**, *103*, 1143-1154. (b) Piloletti, M.; Schlünzen, F.; Harms, J.; Zarivach, R.; Glühmann, M.; Avila, H.; Bashan, A.; Bartels, H.; Auerbach, T.; Jacobi, C.; Hartsch, T.; Yonath, A.; Franceschi, F. *EMBO J.* **2001**, *20*, 1829-1839.

near the A-site (**TET1**, Figure 1.6), where tetracycline may directly prevent aminoacyl tRNA binding via steric hinderance. The $K_d$ for this site is estimated to be between 1 and 20 μM.[26] Five other sites of binding have been proposed,[27b] however the TET5 site is the only other location corroborated crystallographically by more than one study. Molecular dynamics simulations have provided a quantitative description of binding preferences, placing the TET5 site 3 ± 2 kcal/mol higher in energy than TET1.[28] Further, this same study predicts that tetracycline binds in the zwitterionic tautomer at both TET1 and TET5.

[28] Aleksandrov, A.; Simonson, T. *J. Am. Chem. Soc.* **2008**, *130*, 1114-1115.

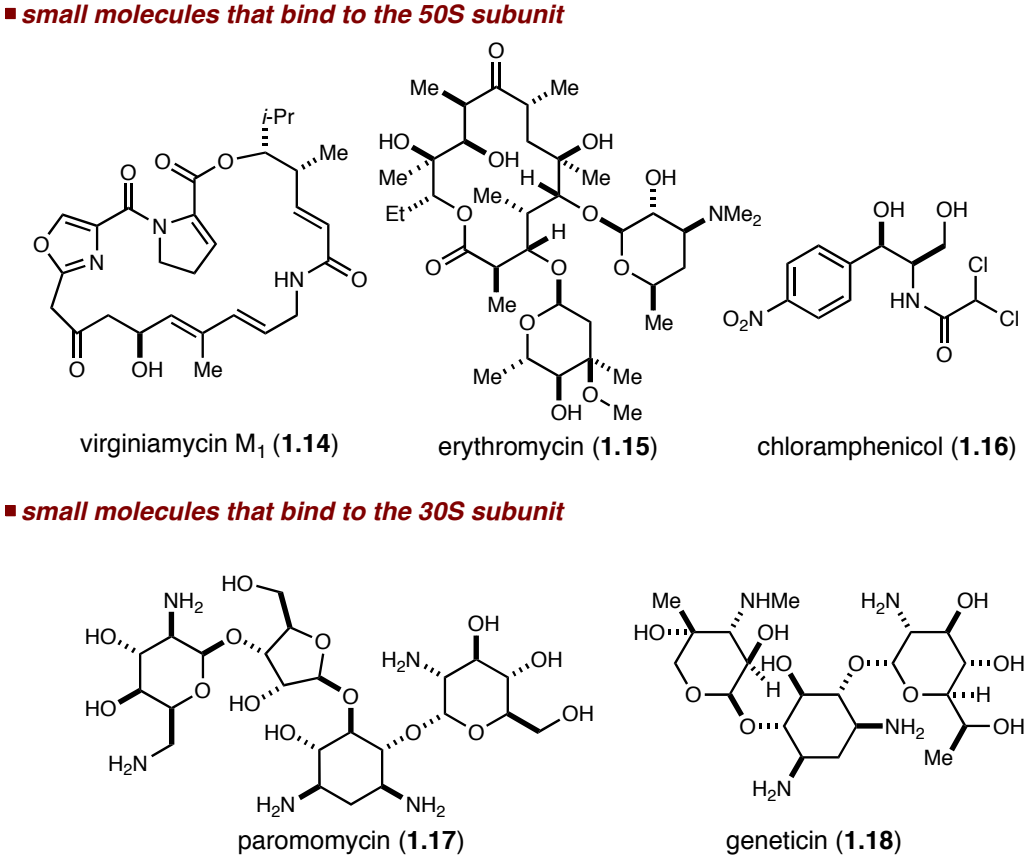


**Figure 1.5** Small molecule natural products target both the 50S and 30S subunits of the bacterial ribosome.

The major contacts made between the 30S subunit at the TET1 site and tetracycline take place in the southern region of the molecule.[27] Of particular importance is the ability for the bridging 1,3-diketone present in the B- and C-rings to bind to $Mg^{2+}$, which in turn makes multiple contacts with the ribosome. Additionally, it is clear that the vinylogous carbamic acid is crucial to bioactivity, as this moiety acts as both a hydrogen bond donor and acceptor. What is most intriguing about the summary of contacts, however, is the lack of contacts made in the northern half of tetracycline. This lack of critical contacts implies that the region can be modified while maintaining bioactivity. Indeed, a survey of

tetracycline natural products confirms this assertion, since much of the variability within the natural product class is present between C5 and C7.

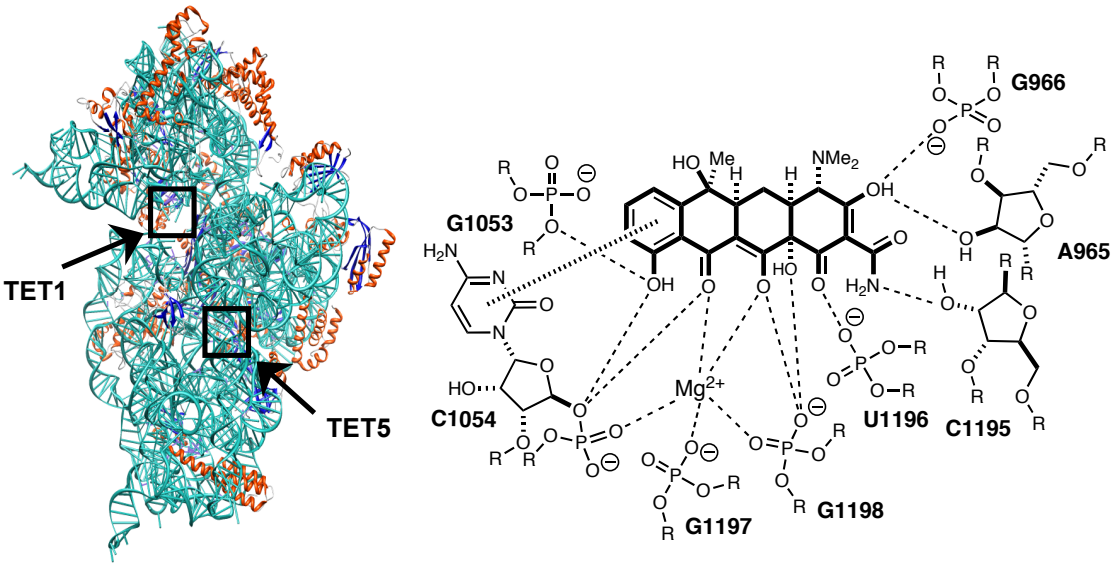


**Figure 1.6** Crystal structure of the 30S subunit of the bacterial ribosome containing tetracycline bound to both the TET1 and TET5 binding sites (left) and major contacts between tetracycline and the TET1 site of the 30s subunit (right).[27a]

## V. Tetracycline Resistance

A collection of *Enterobacteriaceae* accumulated between 1917 and 1954 containing 433 different strains revealed that only 9 (2%) were resistant to tetracycline.[29] This widespread susceptibility coupled with oral availability explains the near immediate application of tetracycline in both clinical and agricultural settings following isolation.[30] Unfortunately, as a result of widespread use, multiple resistance mechanisms have emerged in order for bacteria to combat the effects of the antibiotic. This resistance has reduced the

[29] Hughes, V. M.; Datta, N. *Nature* **1983**, *302*, 725-726.

[30] Chopra, I.; Roberts, M. *Micrbiol. Mol. Biol. Rev.* **2001**, *65*, 232-260.

role of these antibiotics in the treatment of infection, as clinicians now seek other alternatives including second and third generation tetracyclines.[31]

Three distinct types of resistance have emerged to combat the effects of tetracycline in bacteria. The most studied mechanism is resistance by efflux, which involves the transport of an antibiotic out of the cell and away from the ribosome, its cellular target. This form of resistance is comprised of 26 different classes of efflux pumps identified from Gram-positive and Gram-negative bacteria (Figure 1.7).[32] Until literature disclosures in the 1990's, tetracycline was one of the few drugs that suffered efflux-based resistance. Structurally, these pumps are integral membrane proteins that span the lipid bilayer 12-14 times forming a water-filled channel that is typically surrounded by six transmembrane helices.[33] Tetracycline is exported out of the cell while bound to $Mg^{2+}$; this efflux is coupled with proton influx creating a vectoral flow of protons through the channel.[34]

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[31] Roberts, M. C. *FEMS Microbiol. Rev.* **1996**, *19*, 1-24.

[32] Levy, S. B. *Antimicrob. Agents Chemother.* **1992**, *36*, 695-703.

[33] Tamura, N.; Konishi, S.; Yamaguchi, A. *Curr. Opp. Chem. Bio.* **2003**, *7*, 570-579.

[34] Kaneko, M.; Yamaguchi, A.; Sawai, T. *FEBS Letters* **1985**, *193*, 194-198.

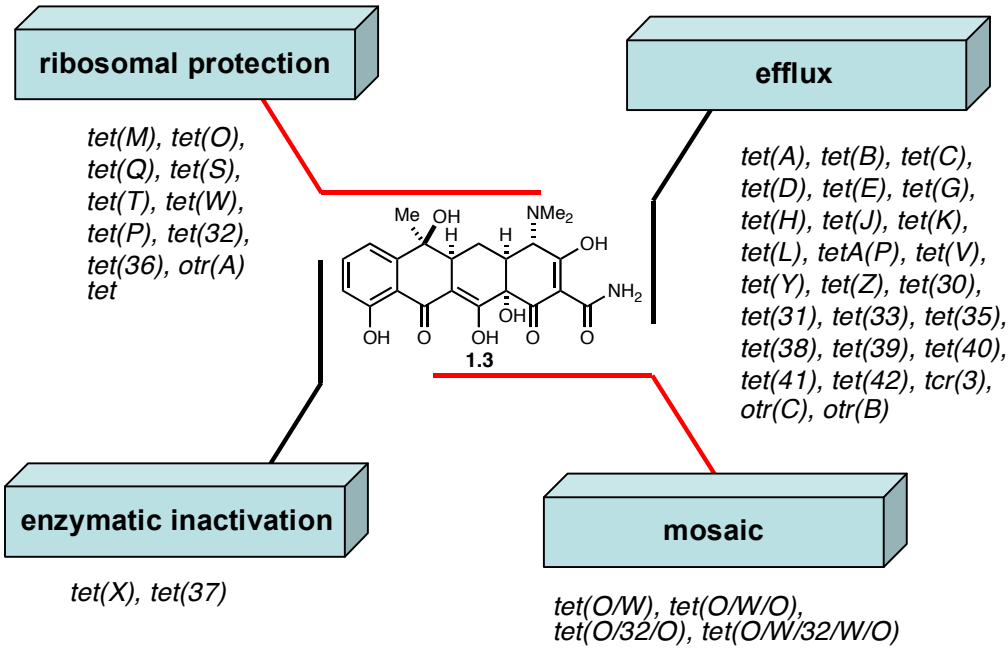


**Figure 1.7** Tetracycline resistance as categorized by mechanism. Genes encoding the resistance proteins are listed below each mode of resistance. Adapted from [35].

The nature of tetracycline efflux protein expression is an important component of our understanding of the bioactivity of the tetracycline antibiotics. Two genes are regulated by tetracycline in organisms capable of tetracycline efflux, one encoding the efflux protein itself and a second encoding a repressor protein.[30] In the absence of tetracycline, the repressor protein binds as a heterodimer to the operators responsible for efflux expression. Thus, these genes remain silenced when tetracycline is not present and the machinery used for its export is not required. However, when tetracycline is in the cellular environment, it may bind to the repressor protein. This binding interaction changes the conformation of the overall heterodimeric structure, greatly reducing binding effi-

[35] Thaker, M.; Spanogiannopoulos, P.; Wright, G. D. *Cell. Mol. Life Sci.* **2010**, *67,* 419-431.

ciency.[36] Once the operator is freed from the repressor protein, transcription may proceed, ultimately enabling the synthesis of necessary efflux proteins.

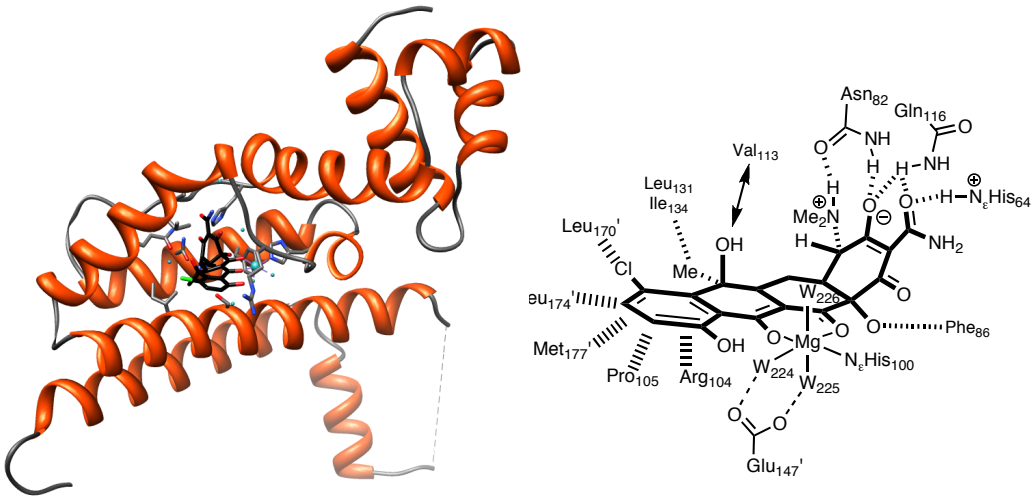


**Figure 1.8** Crystal structure of the $TetR^{D}$-(Cl-Tet)-$Mg^{2+}$ complex and a three-dimensional depiction of important protein/antibiotic interactions.[36]

Beyond efflux, other modes of tetracycline resistance include ribosomal protection[37] and enzymatic inactivation.[38] While less studied, ribosomal protection proteins play a critical role in freeing a distressed ribosome from arrest induced by tetracycline binding. One such protection protein, Tet(O), binds to a location on the distressed ribosome that is quite removed from TET1.[39] Following binding, the protein induces ejection of tetracycline from the ribosome via a mechanism that is not completely understood. However, it is hypothesized that a long-range effect can be induced via an allosteric

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[36] Kisker, C.; Hinrichs, W.; Tovar, K.; Hillen, W.; Saenger, W. *J. Mol. Biol.* **1995**, *247*, 260-280.

[37] Connell, S. R.; Tracz, D. M.; Nierhaus, K. H.; Taylor, D. E. *Antimicrob. Agents Chemother.* **2003**, *47*, 3675-3681.

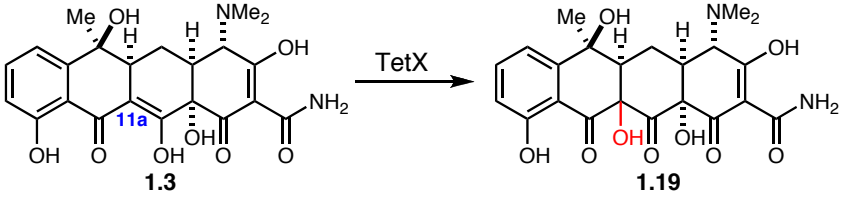
[38] Yang, W.; Moore, I. F.; Koteva, K. P.; Bareich, D. C.; Hughes, D. W.; Wright, G. D. *J. Biol. Chem.* **2004**, *279*, 52346-52352.

[39] Spahn, C. M. T.; Blaha, G.; Agrawal, R. K.; Penczek, P.; Grassucci, R. A.; Trieber, C. A.; Connell, S. R.; Taylor, D. E.; Nierhaus, K. H.; Frank, J. *Mol. Cell* **2001**, *7*, 1037-1045.

mechanism that involves the shifting of helix 34 (h34), causing conformational perturbation near TET1.[39]

The third mechanism of tetracycline resistance used by bacteria, enzymatic inactivation, is the only mechanism that directly reduces the local concentration of an antibiotic since it involves the enzymatic conversion of the molecule to a less effective form. While this is a relatively uncommon mode of resistance for the tetracyclines, it is quite common when one considers other classes of antibiotics such as the β-lactams and aminoglycosides.[38] One such tetracycline inactivating enzyme, TetX, was identified in 1989 from a strain of *Bacteroides fragilis*.[40] This flavin-dependent monooxygenase is proposed to mediate the oxidation of the C11a-position of the tetracycline core structure (Scheme 1.2).[38] Once formed, the sensitive intermediate **1.19** is proposed to undergo decomposition via multiple pathways, one of which involves aromatization of the C-ring.

**Scheme 1.2** Proposed action of the TetX enzyme to induce the decomposition of tetracycline antibiotics.




## VI. Relevant Syntheses

Considering the clinical relevance, resistance challenges, and structural complexity of the tetracycline antibiotics, it is not surprising that these molecules have captured sustained attention by the synthesis community. In the interest of brevity, a detailed summary of the various syntheses of relevant tetracyclines will not be included; rather, the strategic

decisions made in the retrosynthetic deconstruction of the targets will be emphasized.[41] An overview of the syntheses discussed in this section can be found in Figure 1.9.

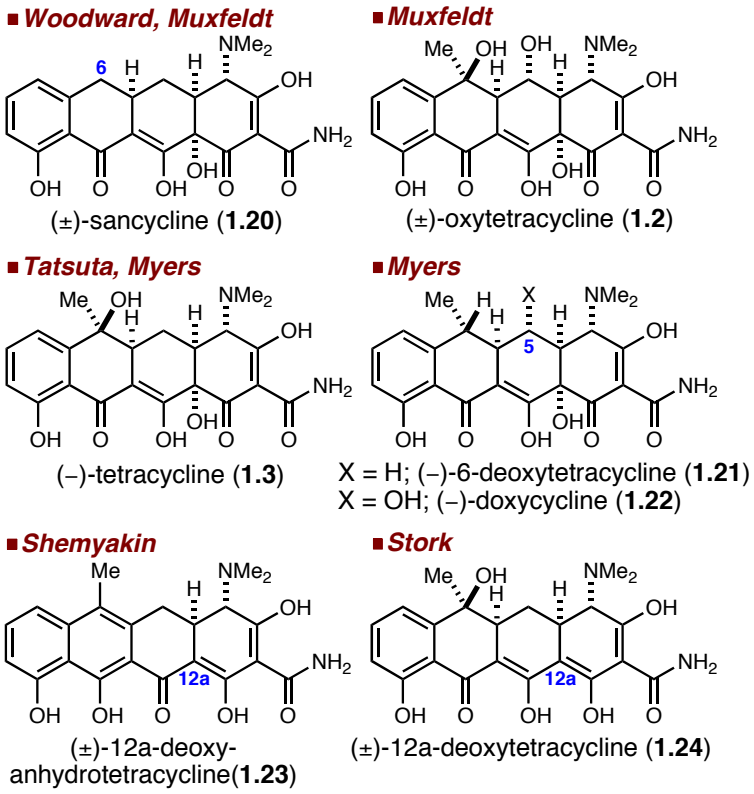



**Figure 1.9** Relevant work towards the synthesis of tetracycline antibiotics.

The initial foray into the total synthesis of a bioactive tetracycline was undertaken by Woodward and co-workers, who disclosed the synthesis of 6-demethyl-6-deoxytetracycline (sancycline, **1.20**, Scheme 1.3) in 1962.[42] This synthesis hinged on the late-stage Dieckmann reaction that was used to synthesize the A-ring of the tetracycline

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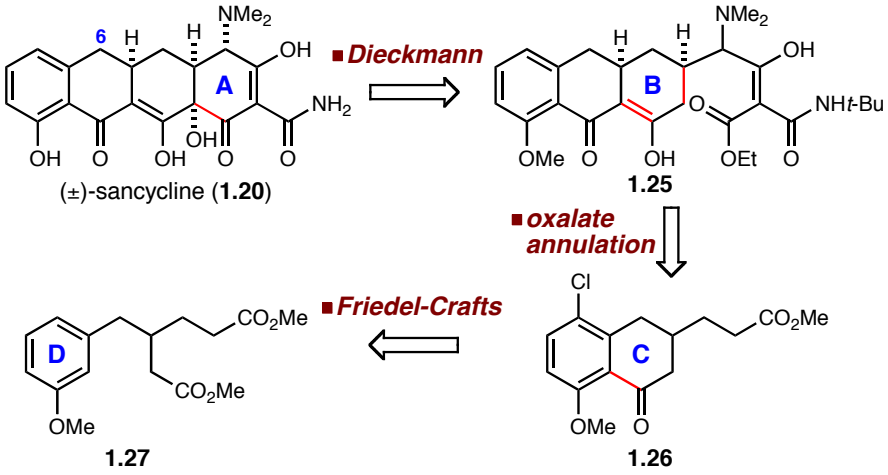
[40] Speer, B. S.; Salyers, A. A. *J. Bacteriol.* **1989**, *171*, 148-153.

[41] For a detailed review of syntheses relevant to the tetracycline antibiotics, please see: Brubaker, J. Ph.D. thesis, Harvard University, 2007.

core structure (**1.25** to **1.20**). This general strategy became an important component of all early syntheses targeting tetracycline-like structures, as it was incorporated in subsequent disclosures by Muxfeldt, Shemyakin, and Stork (*vide infra*). Following retrosynthetic disconnection of the A ring, annulation to form the B-ring was envisioned (**1.26** to **1.25**). In order to effect this transformation, dimethyloxalate was used as a two-carbon synthon, allowing B-ring formation to occur via deprotonation of **1.26** with sodium hydride. Lastly, a Friedel-Crafts acylation was envisioned to form the C-ring (**1.27** to **1.26**). Overall, this synthesis yielded (±)-sancycline in 25 steps and 0.0025% overall yield.

**Scheme 1.3** Key bond disconnections used in the synthesis of (±)-sancycline by Woodward and co-workers.[42]




Soon after the Woodward synthesis, Muxfeldt also completed a synthesis of (±)-sancycline while utilizing an elegant cascade annulation strategy.[43] Following late-stage functionalization (**1.28** to **1.20**), the A- and B-rings of the tetracycline core were targeted.

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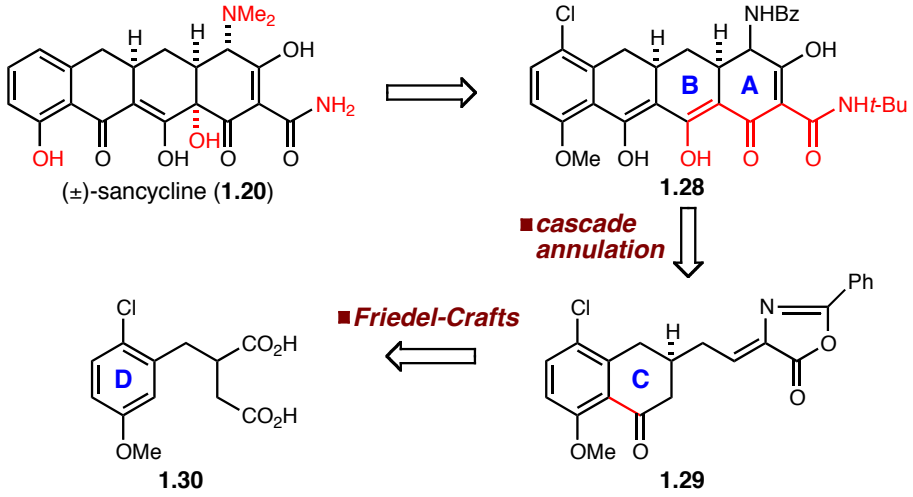
[42] (a) Conover, L. H.; Butler, K.; Johnston, J. D.; Korst, J. J.; Woodward, R. B. *J. Am. Chem. Soc.* **1962**, *84*, 3222-3224. (b) Woodward, R. B. *Pure Appl. Chem.* **1963**, *6*, 561-573. (c) Korst, J. J.; Johnston, J. D.; Butler, K.; Bianco, E. J.; Conover, L. H.; Woodward, R. B. *J. Am. Chem. Soc.* **1968**, *90*, 439-457.

[43] Muxfeldt, H.; Rogalski, W. *J. Am. Chem. Soc.* **1965**, *87*, 933-934.

Utilizing sodium hydride in the presence of *N*-*t*-butyl-3-oxoglutaramate, the conversion of **1.29** to **1.28** proceeded in an extremely efficient process (82% yield). Intermediate **1.29** was then generated in a similar manner to that of the Woodward synthesis (*vide supra*).

**Scheme 1.4** Key bond disconnections used in the synthesis of (±)-sancycline by Muxfeldt and co-workers.[43]




The Muxfeldt synthesis of (±)-sancycline was a precursor to the landmark synthesis of (±)-terramycin in 1968, which is regarded as an amazing achievement in organic synthesis.[44] Conceptually, the same strategy employed in the (±)-sancycline synthesis was employed for the (±)-terramycin synthesis, however terramycin contains added challenges which involve the sensitive C6-tertiary carbinol in addition to the secondary carbinol at C5. Further, the synthesis employed a C12a-hydroxylation reaction that was also developed by Muxfeldt and co-workers for the tetracyclines (**1.31** to **1.2**).[45] To disconnect the

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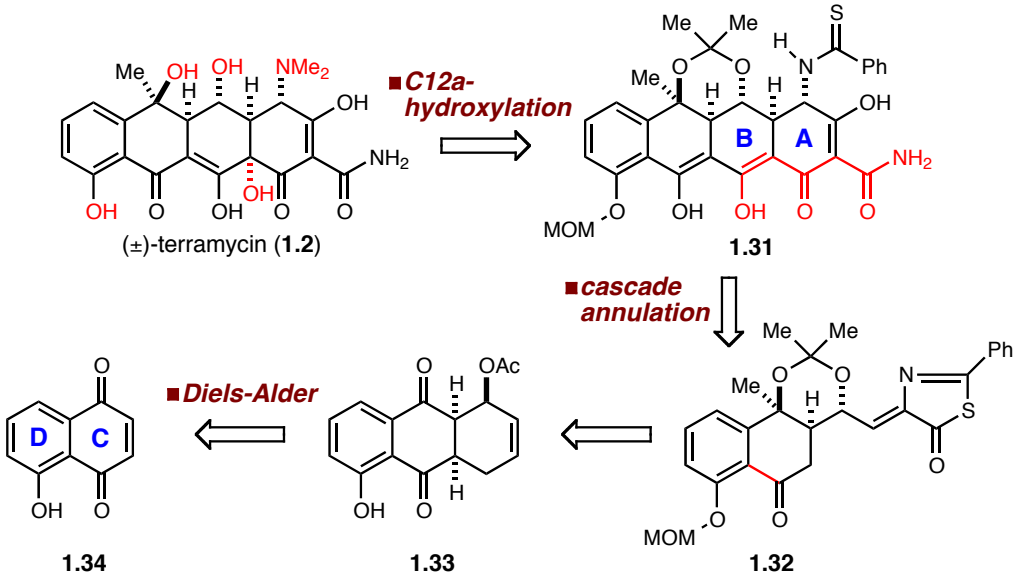
[44] (a) Muxfeldt, H.; Hartmann, G.; Kathawala, F.; Vedejs, E.; Mooberry, J. B. *J. Am. Chem. Soc.* **1968**, *90*, 6534-6536. (b) Muxfeldt, H.; Haas, G.; Hardtmann, G.; Kathawala, F.; Mooberry, J. B.; Vedejs, E. *J. Am. Chem. Soc.* **1979**, *101,* 689-701.

[45] Muxfeldt, H.; Buhr, G.; Banger, R. *Angew. Chem. Int. Ed.* **1962**, *3*, 157.

core tetracyclic framework, a similar cascade annulation reaction was employed to that discussed in the context of (±)-sancycline (Scheme 1.4), this time using thioazolone precursor **1.32**. This precursor was synthesized from juglone (**1.34**) in 16 steps through the intermediacy of **1.33**, which is the Diels-Alder adduct of juglone and 1-acetoxy butadiene.

**Scheme 1.5** Key bond disconnections used in the synthesis of (±)-terramycin by Muxfeldt and co-workers.[44]




In 1966, Shemyakin and co-workers reported the formal total synthesis of tetracycline via means of the synthesis of 12a-deoxy-5a,6-anhydrotetracycline.[46,47] The approach employed to synthesize this degradation product of tetracycline was similar to that of the Woodward (±)-sancycline synthesis because it employed a late-stage Dieckmann reaction to form the A-ring of the tetracycline core. Knoevenagel condensation with

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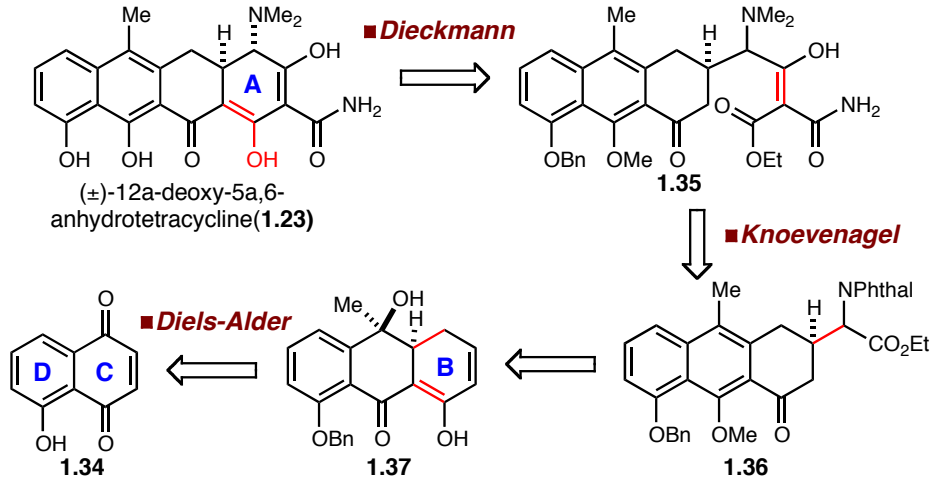
[46] (a) Kolosov, M. .N.; Popravko, S. A.; Shemyakin, M. M. *Lieb. Ann.* **1966**, *668*, 86-91. (b) Gurevich, A. I.; Karapetyan, M. G.; Kolosov, M. N.; Korobko, V. G.; Onoprienko, V. V.; Popravko, S. A.; Shemyakin, M. M. *Tet. Lett.* **1967**, *2*, 131-134.

ethyl ethoxymagnesium malonamate then enabled the conversion of **1.36** to **1.35**. Lastly, in much the same fashion that Muxfeldt utilized a Diels-Alder reaction with juglone, Shemyakin and co-workers targeted the Diels-Alder adduct **1.37**. While 12a-deoxy-5a,6-anhydrotetracycline is a known tetracycline degradation product, no attempt to convert this compound to tetracycline was reported in this literature disclosure.

**Scheme 1.6** Key bond disconnections used in the synthesis of (±)-12a-deoxy-5a,6-anhydrotetracycline by Shemyakin and co-workers.[46]




Stork and co-workers completed a synthesis of (±)-12a-deoxytetracycline in 1996, once again demonstrating the utility of a Dieckmann-based strategy (Scheme 1.7).[48] In this synthesis, formation of the A- and B-rings was targeted via a bis-Dieckmann cyclization. Ultimately this reaction was carried out by subjecting **1.38** to potassium hydride at low temperature, producing **1.24** after hydrogenation of the intermediate product. Intriguingly, a variant of this reaction fails in the absence of the silyl acetal, thus implicating the sensitive C6-tertiary carbinol as the functionality that facilitates decomposition in

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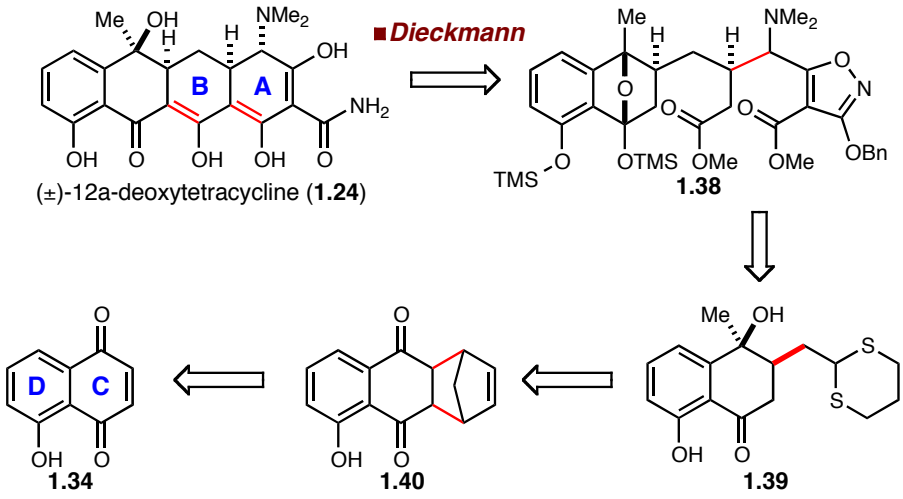
[47] While a formal total synthesis of tetracycline is claimed, later inabilities to effect C12a-hydroxylation with the native stereochemistry at C4 call this claim into question.

[48] Stork, G.; La Clair, J. J.; Spargo, P.; Nargund, R. P.; Totah, N. *J. Am. Chem. Soc.* **1996**, *118*, 5304-5305.

the presence of strong base. Another important feature of this synthesis is the utilization of the Stork-Hagedorn benzyloxy isoxazole.[49] This heterocycle uniquely protects the sensitive vinylogous carbamic acid functional group present within the tetracyclines until it may be unveiled. This work should have yielded a formal synthesis of tetracycline once the C12a-deoxy compound **1.24** had been synthesized. However, Stork and co-workers were unable to reproduce the C12a-functionalization methods described by others in earlier reports.[42,45,50]

**Scheme 1.7** Key bond disconnections used in the synthesis of (±)-12a-deoxytetracycline by Stork and co-workers.[48]




Surprisingly, tetracycline itself did not succumb to total synthesis until 30 years after the Muxfeldt terramycin synthesis. It was Tatsuta and co-workers who were the first to synthesize tetracycline, disclosing their work in 2000 (Scheme 1.8).[51] Retrosynthetically, the first strategic decision made in the synthesis was to delay installation of the

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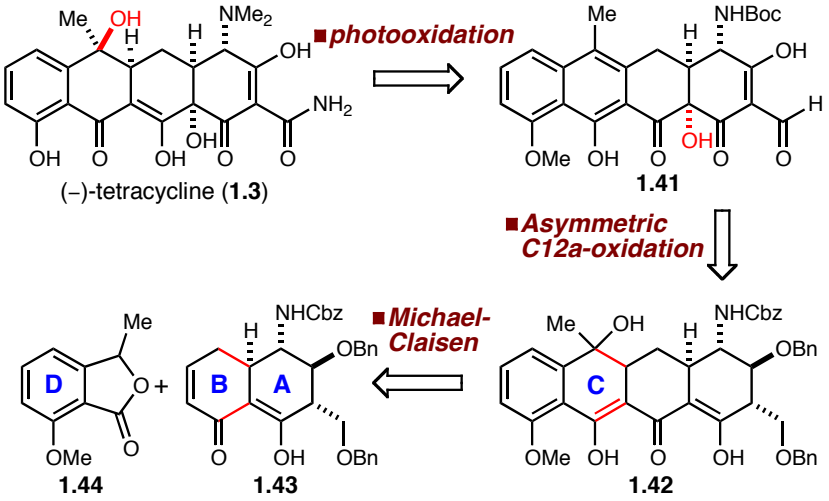
[49] Stork, G.; Hagedorn III, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 3609-3611.

[50] (a) Holmlund, C. E.; Andres, W. W.; Shay, A. J. *J. Am. Chem. Soc.* **1959**, *81*, 4748-4749. (b) Photochemical oxidation of tetracycline: Davies, A. K.; McKellar, J. F.; Philips, G. O.; Reid, H. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 368-375.

C6-tertiary carbinol until the final stage of the synthesis. This not only allowed more inert 5a-6-anhydro-intermediates to be carried through much of the synthesis, but it also relied upon a highly precedented oxidation since both Scott[52] and Wasserman[53] had studied similar reactions earlier. The most intriguing component of the synthesis, however, was the utilization of isobenzenefuranone **1.44** in a Michael-Claisen reaction. In this reaction, the benzylic position of **1.44** was deprotonated with LDA at low temperature, and coupled with enone **1.43** to effect annulation of the C-ring **(1.42)**. Lastly, AB synthon **1.43** was synthesized in 12 steps from D-glucosamine.

**Scheme 1.8** Key bond disconnections used in the synthesis of (–)-tetracycline by Tatsuta and co-workers.[51]




## VII. The Myers Route to Fully Synthetic Tetracyclines

The first generation of tetracycline antibiotics used clinically were the natural products themselves. However, as resistance emerged, newer semisynthetic tetracyclines were

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[51] Tatsuta, K.; Yoshimoto, T.; Gunji, H.; Okado, Y.; Takahashi, M. *Chem. Lett.* **2000**, 646-647.

[52] Scott, A. I.; Bedord, C. T. *J. Am. Chem. Soc.* **1962**, *84*, 2271-2272.

[53] Wasserman, H. H.; Lu, T.-J. *J. Am. Chem. Soc.* **1986**, *108*, 4237-4238.

created in response. This led to the semisynthesis of minocycline (**1.45**) and doxycycline (**1.22**), two drugs that have been widely used by clinicians (Figure 1.10).[35] Ultimately, this was followed by the third generation of tetracycline antibiotics, the glycylcyclines, as exemplified by tigecycline (**1.46**). Yet, these too are semisynthetic antibiotics, obtained from the derivitization of minocycline.[54] It is not until recently that the accessibility of structurally diverse tetracyclines has dramatically improved.

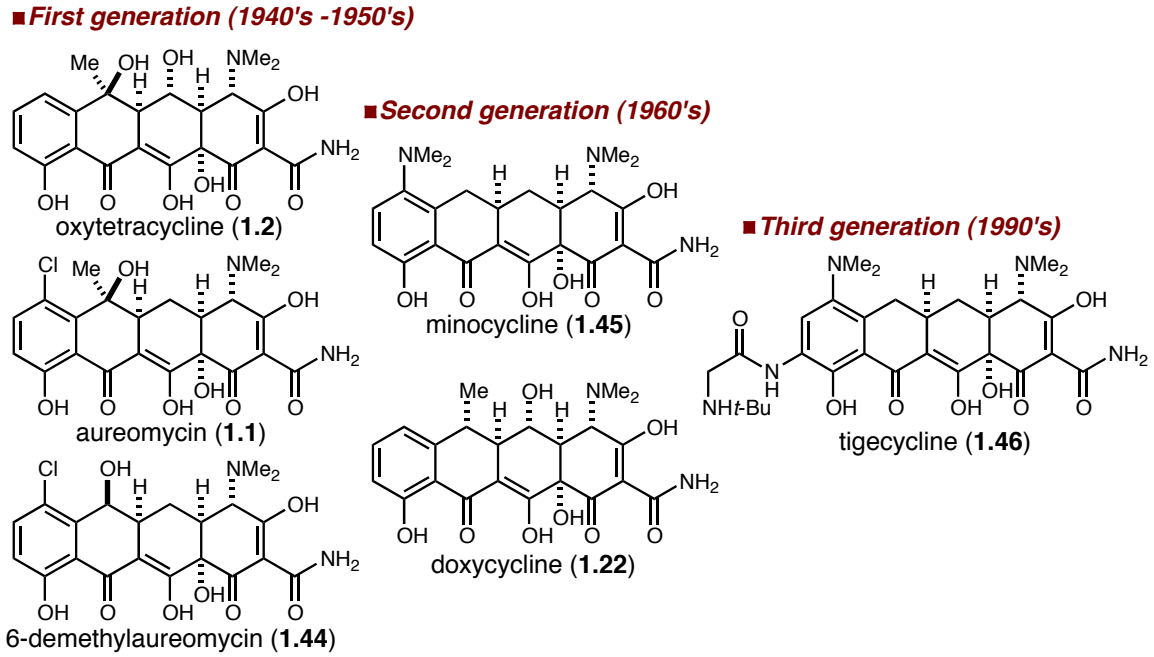


**Figure 1.10** The evolution of clinically used tetracycline antibiotics.[35]

In 2005, Myers and co-workers reported the synthesis of (–)-tetracycline via an exceedingly efficient sequence comprised of 17 steps from benzoic acid in 1.1% yield.[55] This was a remarkable improvement over the previous tetracycline synthesis completed

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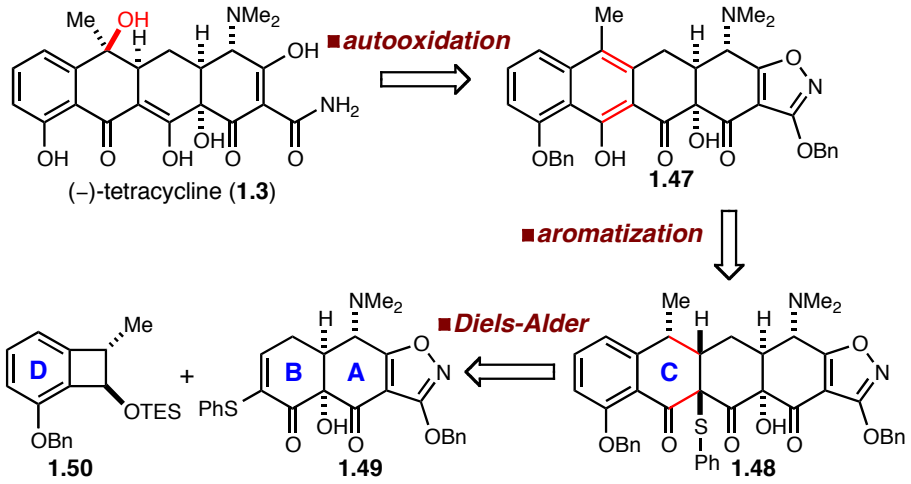
[54] Sum. P.-E.; Lee, V. J.; Testa, R. T.; Hlavka, J. J.; Ellestad, G. A.; Bloom, J. D.; Gluzman, Y.; Tally, F. P. *J. Med. Chem.* **1994**, *37*, 184-188.

[55] Charest, M. G.; Siegel, D. R.; Myers, A. G. *J. Am. Chem. Soc.* **2005**, *127*, 8292-8293.

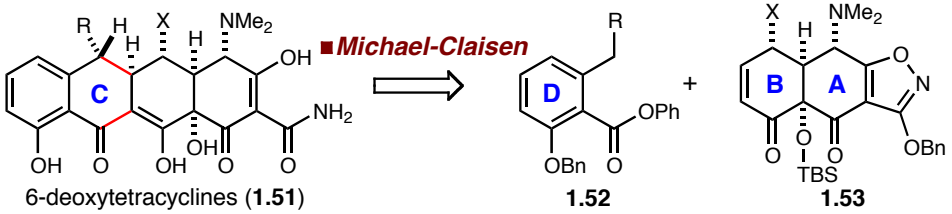
by Tatsuta and co-workers, which required 34 steps and had an overall yield of 0.002%. The strategy that was employed relied upon the late-stage autooxidation of naphthol **1.47**, followed by hydrogenation (Scheme 1.9). In order to obtain intermediate **1.47**, a sulfoxide elimination was envisaged, thus requiring sulfide **1.48** as the immediate precursor. In the key fragment coupling reaction, which would form the C-ring of the tetracycline core, a Diels-Alder reaction was employed using triethylsilyloxybenzocyclobutene derivative **1.50** and A,B-enone **1.49**. Unlike the Tatsuta synthesis, Myers and co-workers chose to implement the Stork-Hagedorn benzyloxy isoxazole, which dramatically reduced the number of manipulations required to produce the requisite vinylogous carbamic acid function. Additionally, the late-stage hydrogenation to set the C5a-stereocenter also deprotected the benzyl protecting groups, making the final sequence from naphthol **1.47** to tetracycline remarkably efficient.

**Scheme 1.9** Key bond disconnections used in the synthesis of (–)-tetracycline by Myers and co-workers.[55]



A contemporaneous literature disclosure also by Myers and co-workers fundamentally change the way that new tetracyclines are developed as it revealed a general approach to synthetic 6-deoxy analogs of this natural product class.[56] Using a convergent strategy that employed the use of A,B-enone **1.53** and potentially modifiable D-ring esters, the 6-deoxy-tetracycline core structure may be obtained in a single efficient reaction (Scheme 1.10). Since crystal structures of tetracycline bound to the bacterial ribosome have revealed the lack of significant contacts in both the northern region and eastern region of the molecule (*vide supra*), this strategy is ideal to produce analogs with improved antibacterial activity. Following this powerful new strategy, Myers and co-workers have disclosed further efforts to streamline the process and provide access to an even larger subset of tetracycline analogs.[57]

**Scheme 1.10** Key annulation used in the synthesis of 6-deoxytetracycline analogs by Myers and co-workers.[56]




## VIII. Tetracycline Synthesis Strategy

With an outline of past tetracycline syntheses now complete, it is useful to conceptualize the approaches. While each of the synthesis plans outlined in sections VI and VII are dis-

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[56] Charest, M. G.; Lerner, C. D.; Brubaker, J. D.; Siegel, D. R.; Myers, A. G. *Science* **2005**, *308*, 395-398.

[57] (a) Brubaker, J. D.; Myers, A. G. *Org. Lett.* **2007**, *9*, 3523-3525. (b) Sun, C.; Wang, Q.; Brubaker, J. D.; Wright, P. M.; Lerner, C. D.; Noson, K.; Charest, M.; Siegel, D. R.; Wang, Y.-M.; Myers, A. G. *J. Am. Chem. Soc.* **2008**, *130*, 17913-17927. (c) Kummer, D. A.; Li, D.; Dion, A.; Myers, A. G. *Chem. Sci.* **2011**, *2*, 1710-1718. (d) Wright, P. M.; Myers, A. G. *Tetrahedron* **2011**, *67*, 9853-9869.

tinct, they each display a bias towards the linear construction of the naphthacene core. More specifically, early approaches to the tetracyclines by Woodward, Muxfeldt, Shemyakin, and Stork involve the stepwise introduction of rings via Claisen reaction, starting from the D-ring; this represents D- to A-ring directionality (Figure 1.11). More recently, Tatsuta and Myers have used a Michael-Claisen (or Diels-Alder) reaction to effect the annulation of the C-ring; this represents the inverse, A- to D-ring directionality. While *a priori* it is not obvious which approach is superior, certainly the literature disclosures by Myers reveal that the latter approach currently is most practical. Further, A- to D-ring directionality allows the assemblage of a single, unvarying eastern region; this is ideal considering these functionalities are crucial for bioactivity and therefore cannot be altered.

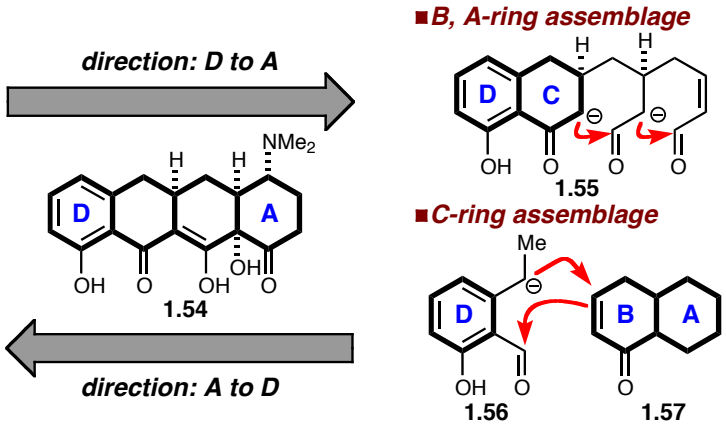


**Figure 1.11** Previous tetracycline syntheses employ a linear introduction of the rings.

### IX. A Macrocyclic Approach to Polycyclic Structures

Progress in the field of organic synthesis is made with discoveries in three major areas: (1) new chemical reactions; (2) improved reaction conditions; and (3) novel synthesis

strategies.[58] The experimental results disclosed in Chapters 2-4 summarize our efforts to further a synthesis strategy. Yet, in doing so, we hope that the reader will also be convinced that important discoveries have ultimately been achieved in all three areas, considering the development of a synthesis strategy requires execution of new reactions in previously unexplored situations.

To introduce the concept of synthesis strategy, it is instructive to consider initially a strategy established by R. B. Woodward and co-workers in the context of erythromycin (Scheme 1.11).[59] Within this synthesis, an initial dithioacetal was used to produce a bicyclic ring system containing a stereocenter at the ring fusion. This single stereocenter was then utilized to control the formation of three additional stereocenters via ketone reduction and olefin dihydroxylation to produce **1.59**. Intermediate **1.59** was then utilized as a common building block for the synthesis of both **1.60** and **1.61**, two fragments that were later coupled and elaborated to produce erythromycin.

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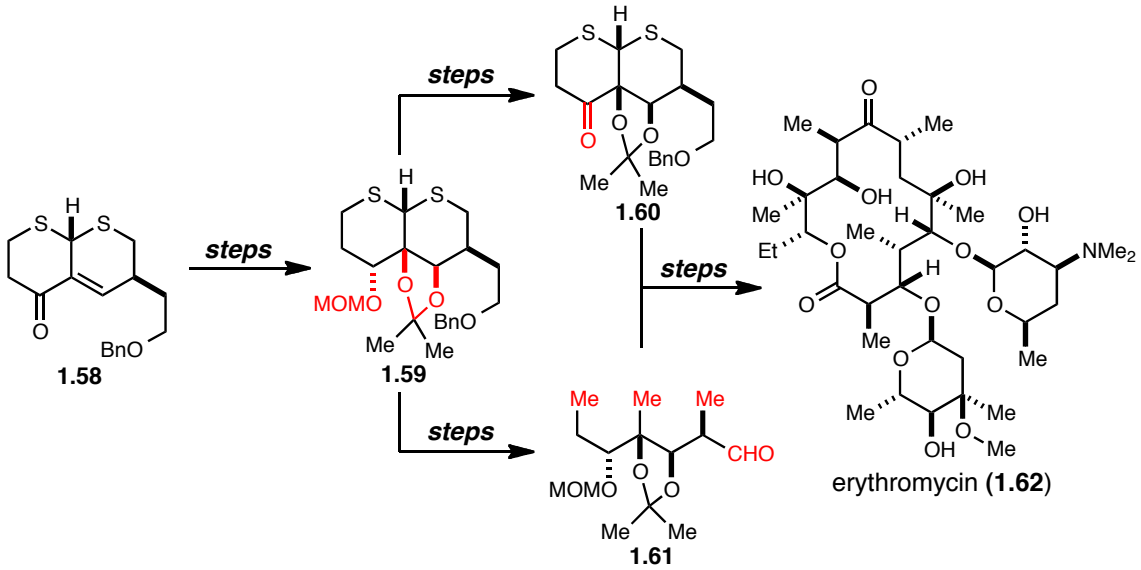
[58] Deslongchamps, P.; *Aldrichimica Acta* **1984**, *17*, 59-71.

[59] Woodward, R. B. *et al. J. Am. Chem. Soc.* **1981**, *103*, 3210-3213.

**Scheme 1.11** Overview of the erythromycin synthesis completed by Woodward and co-workers.




Scrutiny of the strategy employed in the synthesis of erythromycin reveals the implimentation of fused ring systems for stereocontrol in the synthesis of a macrocyclic natural product.[60] In other words, Woodward connected methods of cyclic stereocontrol to the synthesis of acyclic or macrocyclic natural products, an approach that was advantageous in an era of organic synthesis with limited methods of acyclic stereocontrol (Figure 1.12). Some time ago, the Evans group began a research program aimed at the assessment of a fundamentally different synthesis strategy than that employed by Woodward and co-workers. Instead of targeting acyclic structures, we sought to redefine how polycyclic target structures are constructed. In contrast to the Woodward strategy, this strategy sought to connect powerful methods of acyclic stereocontrol to the synthesis of polycycles through the intermediacy of a macrocycle. In doing so, this forces the analy-

[60] Acyclic natural products and macrocyclic natural products are considered to be of the same general architectural category since a macrocyclic natural product is merely a macrocyclization step beyond being acyclic.

sis of reactivity and stereochemical transmission within a macrocyclic setting, which is an arena of heightened complexity.

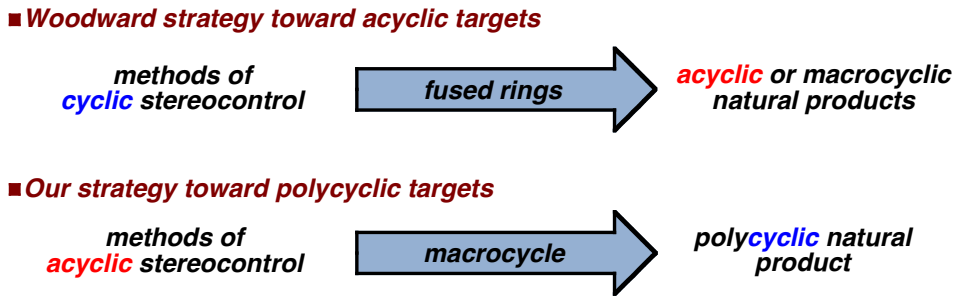



**Figure 1.12** Graphical depiction of the two synthesis strategies.

Deslongchamps was among the first to demonstrate that a macrocyclic approach to polycyclic targets is an entirely reasonable strategy via application of the transannular Diels-Alder reaction.[61] In complementary studies, Still demonstrated that conformational analysis of chiral macrocycles affords predictable levels of intermolecular asymmetric induction.[62] Collectively, these observations deserve recognition in the evolution of approaches towards the synthesis of polycyclic structures. In an effort to expand and systematize this strategy, the Evans group has employed it in the total synthesis of three structurally distinct natural products to date: salvinorin A (**1.63**), (–)-FR182877 (**1.64**), miyakolide (**1.65**, Figure 1.13).[63]

---

[61] (a) Deslongchamps, P. *Pure and Appl. Chem*. **1992**, *64*, 1831-1847. (b) Marsault, E.; Toró, A.; Nowak, P.; Deslongchamps, P. *Tetrahedron* **2001**, *57*, 4243-4260.

[62] Still, W. C.; Galynker, I. *Tetrahedron* **1981**, 37, 3981-3996.

[63] (a) Evans, D. A.; Ripin, D. H. B.; Halstead, D. P.; Campos, K. R. *J. Am. Chem. Soc.* **1999**, 121, 6816-6826. (b) Evans, D. A.; Starr, J. T. *J. Am. Chem. Soc.* **2003**, 125, 13531-13540. (c) Scheerer, J. R.; Lawrence, J. F.; Wang, G. C.; Evans, D. A. *J. Am. Chem. Soc*. **2007**, 129, 8968-8969.

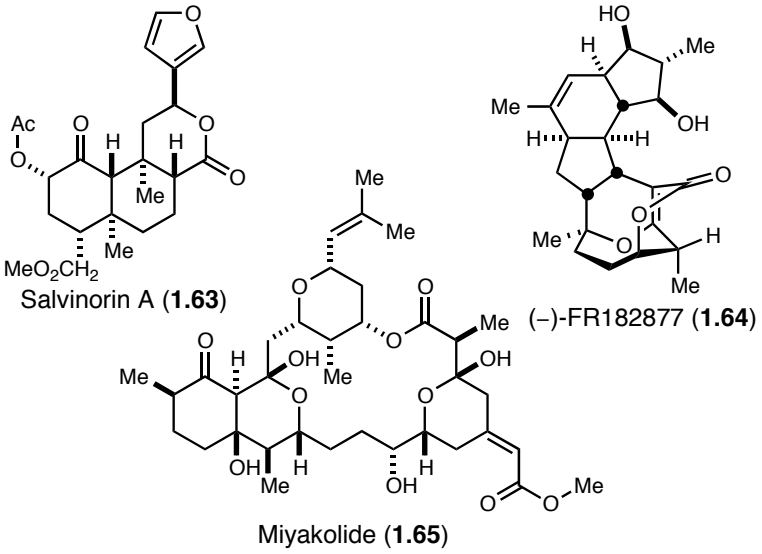



**Figure 1.13** Natural products synthesized by Evans and co-workers while employing a macrocyclic approach.[63]

To conceptualize the macrocyclic approach to polycyclic target structures, it is best to consider initially the larger Evans group research program. Over the past four decades, the Evans group has looked to establish methods for stereocontrolled carbon-carbon bond formation in acyclic settings.[64] This has led to considerable advances in the construction of polyacetate- and polypropionate natural products in particular. Further, these methods have been validated via implementation within numerous syntheses, including the biosynthetic precursor to monensin, premonsin (**1.66**), which was synthesized by Evans and co-workers in 1986 (Scheme 1.12).[65] Within that synthesis, aldol methodology was extensively employed, producing premonensin as the direct result of the work.

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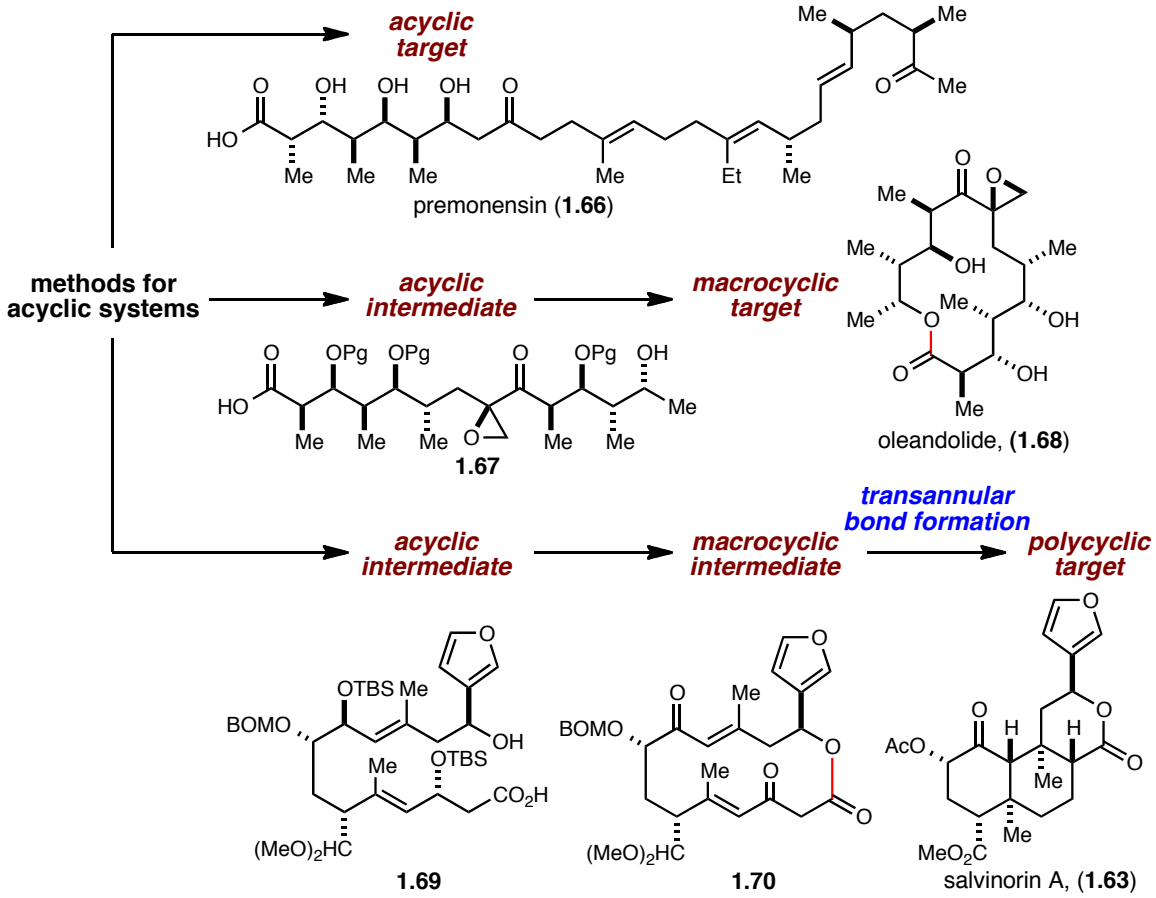
[64] Considerable advances have been made in cyclic settings as well, however this is less pertinent to the discussion at hand.

[65] Evans, D. A.; DiMare, M. *J. Am. Chem. Soc.* **1986**, *108*, 2476-2478.

**Scheme 1.12** Overview of the Evans group synthesis philosophy towards architecturally distinct target structures.




Total synthesis of macrolide antibiotics represents an extension of the strategy employed to synthesize premonensin. Specifically, in the synthesis of the macrolide antibiotic aglycone oleandolide, aldol methodology was extensively employed to synthesize seco-acid **1.67**.[66] This acyclic intermediate was then utilized in a macrocyclization reaction, ultimately producing the natural product after deprotection. Thus, the beginning phase for the synthesis of both premonensin and oldeandolide, two architecturally distinct natural products, was the same: acyclic stereocontrol to generate an acyclic molecule. It

[66] Evans, D. A.; Kim, A. S.; Metternich, R.; Novack, V. J. *J. Am. Chem. Soc.* **1998**, *120*, 5921-5942.

was in the latter stage of the oleandolide synthesis that the strategies deviated.

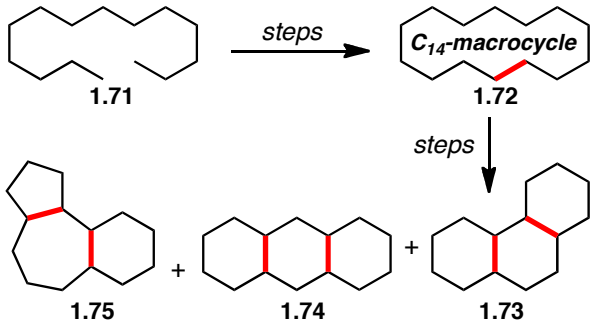
The macrocyclic approach toward polycyclic natural products represents an extension of the strategy employed for the synthesis of oleandolide. The total synthesis of salvinorin A serves as an important example of the successful implementation of this strategy.[63c] This synthesis specifically targeted macrocycle **1.70**, which was synthesized via the generation of an acyclic intermediate (**1.69**), followed by macrocyclization. Once formed, the macrocycle was used in an elegant trasannular cascade, ultimately producing the core of salvinorin A. Subsequent functionalization produced the natural product itself.

The completed salvinorin A synthesis is important for several reasons. First, it shows that the construction of polycyclic structures does not need to be dominated by intermolecular annulation reactions at the expense of the implementation of methods designed for acyclic settings. Secondly, it demonstrates that a rationally designed macrocycle can be a tremendous asset in complex molecule synthesis as exemplified by the transannular cascade that was both remarkably stereoselective and efficient. A reasonable criticism of the strategy is that it purposefully invokes the intermediacy of a macrocycle, which is a notoriously difficult entity to construct. I argue that given the plethora of methods now developed for previously difficult macrocyclizations, these large-rings should be perceived as an asset within the context of a synthesis endeavor rather than a liability.

The work presented within this thesis, which targets tetracycline for synthesis, is considered the fourth example of an intramolecular annulation strategy from our group. Generally speaking, the synthesis of tetracycline can be viewed as a "two-bond problem" when one considers the formation of two transannular bonds from a C14-macrocycle

(Scheme 1.13).[67] Thus, our task was to devise an appropriately functionalized macrocycle such that stereoselective, late-stage transannular bond formation may occur to produce the tetracycline core (**1.74**). It should be mentioned that the tetracycline project is only a component of a larger program aimed at the synthesis of target structures from C14-macrocycles. Extension to other natural products with 6-6-6 (**1.73**) or 5-7-6 (**1.75**) ring systems from similar C14-macrocycles is also feasible with this approach

**Scheme 1.13** Potential ring systems that can be accessed from a C14-macrocycle.

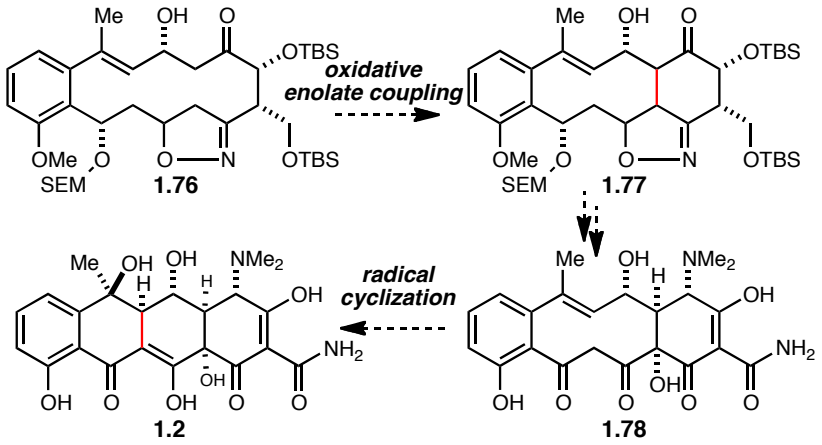



**X. Project History within the Evans group**

In 2004, Dr. Ioannis Sapountzis commenced a synthesis project in the Evans group targeting (–)-oxytetracycline (Scheme 1.14). Initial efforts targeted macrocycle **1.76**, a substrate that was envisioned to undergo oxidative enolate coupling to form **1.77**. Elaboration of **1.77** to advanced intermediate **1.78** would set the stage for the last C-C bond forming reaction of the synthesis, a radical cascade. Sapountzis was able to synthesize macrocycle **1.76**, however was unable to achieve transannular C-C bond formation.

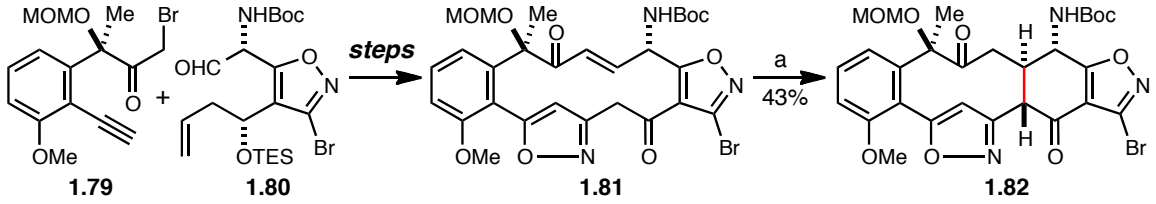
[67] The term C14-macrocycle refers to 14-membered carbocyclic macrocycles.

**Scheme 1.14** Strategy employed by Sapountzis towards (–)-oxytetracycline.




Stimulated by the arrival of Dr. Thomas Knöpfel to the Evans group, a second-generation route was proposed (Scheme 1.15). Fragments **1.79** and **1.80** were initially synthesized without my assistance. Upon my entrance into the Group, we scaled-up the synthesis of both fragments and elaborated these intermediates to macrocycle **1.81**. Ultimately, we validated a transannular Michael strategy via execution of the reaction from **1.81** to **1.82** employing inferior conditions that are no longer used (*vide infra*). Following the departure of Dr. Knöpfel, I redesigned the fragments in the pursuit of a viable synthesis, resulting in the material discussed in Chapters 2-4.[68]

**Scheme 1.15** Work performed with Dr. Thomas Knöpfel in an early approach to (–)-tetracycline.




Reagents and conditions: (a) LiOMe, $LiClO_4$, THF, –8 °C; 43%.

[68] While macrocycle **1.81** is considered the first macrocycle of its kind, for the purposes of this thesis, macrocycle **2.3** in chapter 2 will be considered the first generation of this route. This distinction is made since further generations that directly correspond to **2.3** will follow in chapters 3 and 4.

# *Chapter 2*

## Synthesis of the First Generation Macrocycle

### I. Synthesis Plan

Tetracycline, by nature of the location and number of functional groups within the molecule, is prone to decomposition via multiple pathways, often involving the C6 tertiary carbinol.[7d,69] Therefore, stabilization of this functional group is critical to the viability of a synthesis plan that requires its presence (*vide infra*). We envisioned replacement of the C5a-hydrogen with a hydroxyl function, reducing the propensity for intermediates to aromatize (Scheme 2.1). In turn, this requires a late-stage reduction of the C5a tertiary carbinol to introduce the requisite C5a stereogenic center in the final steps to the target. In order to further stabilize late-stage intermediates, we chose to protect the bridging 1,3-diketone of the C- and B-rings as an isoxazole, which also may be cleaved via reduction. Thus, it was initially envisioned that both C5a- and isoxazole reduction could be coupled into a single reduction cascade transforming **2.1** to **1.3**.[70]

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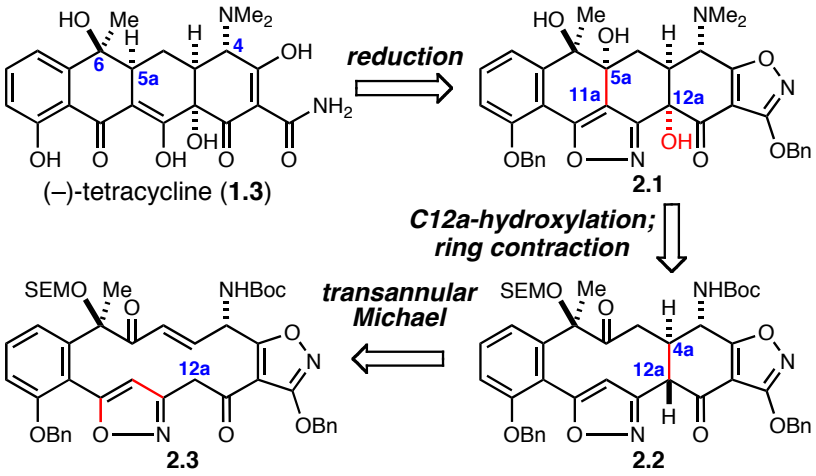
[69] For a more detailed description of the decomposition pathways, please see chapter 1, section III.

[70] This putative reduction cascade is undoubtedly a challenging transformation, however its feasibility is supported by precedent from the Myers synthesis of tetracycline (see ref. [55]). In that case, an alkylidine-1,3-diketone intermediate was accessed and subsequently hydrogenated from the convex face. In

**Scheme 2.1** Synthesis plan to (–)-tetracycline.




We next identified the C5a-C11a bond as a key retrosynthetic disconnection. Constrained within a 10-membered ring, we anticipated that the electron-rich isoxazole placed opposite the ketone would undergo a substitution reaction in the presence of a mild Lewis acid. The stereochemical outcome, while ultimately inconsequential, was presumed to arrive from a macrocyclic conformation that places the C6 tertiary carbinol and the C5a ketone anti to one another based upon a dipole minimization model. Installation of the C12a hydroxyl function was envisioned to arise from oxidation of an enolate derived from intermediate **2.2**. Admittedly, at the outset of this work it was unclear what bias the 10-membered ring might exhibit, yet given the plethora of established enolate hydroxylation methods, this oxidation was considered achievable.[71]

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our synthesis plan, a similar intermediate should be accessed upon reductive cleavage of the isoxazole and ejection of the C5a-hydroxyl function.

[71] For select examples of α-ketone oxidation via silyl enol ether intermediates, see: (a) Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tet. Lett.* **1974**, *49*, 4319-4322. (b) Rubottom, G. M.; Marrero, R. *J. Org. Chem.* **1975**, *40*, 3783-3784. (c) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599-1602. (d) McCormick, J. P.; Tomasik, W.; Johnason, M. W. *Tet. Lett.* **1981**, *22*, 607-610. (e) Andriamialisoa, R. Z.; Langois, N.; Langlois, Y. *Tet. Lett.* **1985**, *26*, 3563-3566. (f) Becicka, B. T.; Koerwitz, F. L.; Drtina, G. J.; Baenziger, N. C.; Wiemer, D. F. *J. Org. Chem.* **1990**, *55*, 5613-5619. For select examples of α-ketone oxidation of enolates, see: (a) Davis, F. A.; Chen, B. *Chem. Rev.* **1992**, *92*, 919-934. (b) Ishi-

Lastly, we targeted the C12a-C4a ring fusion. It was envisioned that selective enolization of intermediate **2.3** would enable a transannular Michael addition, forming the A-ring and setting the C4a-stereocenter. The C12a-stereocenter is inconsequential, since this position is later hydroxylated (*vide supra*). Assuming ground state conformational preferences translate to the transition state in this reaction, the stereochemical outcome will rely on the macrocyclic conformation of the enolate derived from intermediate **2.3**. Considering both stereocenters present within the macrocycle are proximal to the enone acceptor, they will undoubtedly play a critical role in the success or failure of this transformation (Figure 2.1). *A priori*, it was predicted that both the C6- and C4-stereocenters would be mutually reinforcing, as the former allows dipole minimization, and the latter places the bulky NHBoc group in the pseudoequatorial position (**2.5**). Yet, intriguing questions as to the extent of interplay between the two resident stereocenters remained unanswered with simplistic models. Thus, we sought to answer these questions via execution of our synthesis plan.

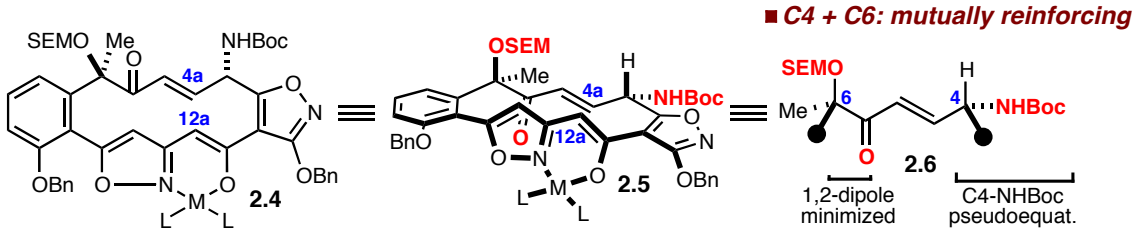


**Figure 2.1** *A priori* conformational prediction justifies the synthesis of macrocycle **2.3**.

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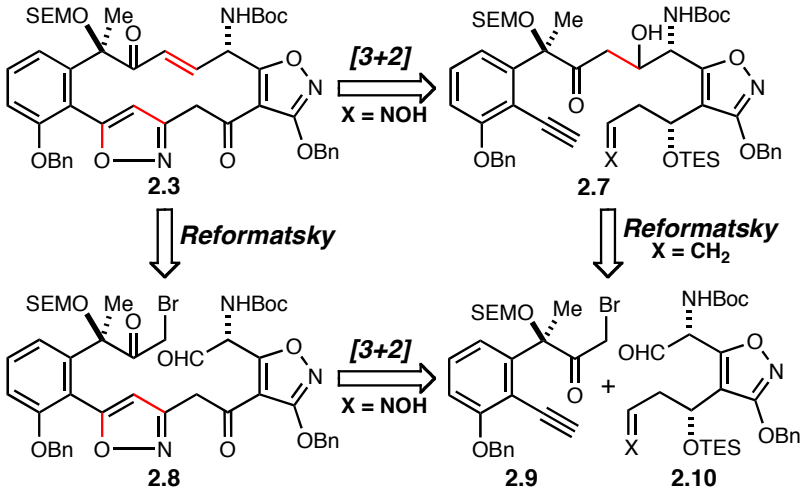
maru, T.; Shibata, N.; Nagai, J.; Nakamura, S.; Toru, T.; Kanemasa, S. *J. Am. Chem. Soc.* **2006**, *128*,

## II. Macrocycle Synthesis

To maximize convergence, two key disconnections were targeted for the synthesis of macrocycle **2.3**, namely a nitrile-oxide[72] cycloaddition and a samarium-diiodide promoted Reformatsky[73] aldol (Scheme 2.2). Due to the orthogonality of the functional groups required for each of these transformations, in principle, we had two options for this step-wise annulation. Since fragments **2.9** and **2.10** are of roughly equal complexity, it was initially anticipated that a Reformatsky fragment coupling, followed by nitrile-oxide macrocyclization, would be the most efficient sequence.[74] With this plan in mind, we embarked upon the synthesis of the requisite fragments.

**Scheme 2.2** Synthesis plan towards C14-macrocycle **2.3**.




16488-16489.

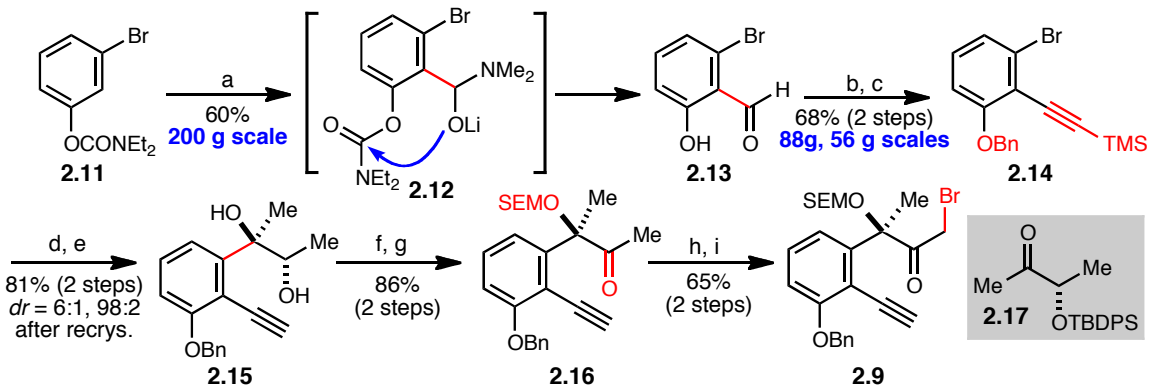
[72] Huisgen, R. *Angew. Chem. Int. Ed.* **1963**, *2*, 565-632.

[73] Reformatsky, S. *Berichte der deutschen chemischen Gesellschaft.* **1887**, *20*, 1210-1211.

[74] Intermolecular nitrile-oxide cycloadditions are typically performed with an excess of one coupling partner since dimerization of the nitrile-oxide is a common biproduct. For select examples of intermolecular nitrile-oxide cycloadditions, see: (a) reference 63a; (b) Dondoni, A.; Giovannini, P. P.; Massi, A. *Org. Lett.* **2004**, *6*, 2929-2932. (c) Schmitt, D. C.; Lam, L.; Johnson, J. S. *Org. Lett.* **2011**, *13*, 5136-5139.

The synthesis of the western fragment **2.9** began with known diethylcarbamate protected 3-bromophenol (**2.11**, Scheme 2.3).[75] Selective *ortho*-lithiation[76] followed by dimethylformamide quench furnished versatile trisubstituted bromosalicaldehyde **2.13** in two steps from commercially available material in 60% yield on a 200 g scale. Incorporation of an *in situ* cleavage of the carbamate protecting group was inspired by an observation made by Snieckus and co-workers in a related system, however it was not utilized to the full synthetic potential in that scenario.[76] Decomposition of the protecting group most likely proceeds through the intermediacy of DMF adduct **2.12**, which may facilitate carbamate migration to liberate the stabilized lithium phenolate. Importantly, the established procedure is a marked improvement compared with prior art, which utilizes an unselective Reimer-Tiemann reaction[77] or metallation of protected anisaldehyde.[78]

**Scheme 2.3** Synthesis of the western fragment **2.9**.




Reagents and conditions: (a) LDA, DMF, THF, –78 °C; 60%; (b) BnBr, $K_2CO_3$, DMF, rt; (c) LDA, $TMSCHN_2$, THF, –78 °C to rt; LDA, TMSCl, –78 °C; 68%, (2 steps); (d) *n*-BuLi, **2.17**, THF, –78 °C; (e) TBAF, THF, 0 °C to rt; 81% (2 steps); (f) $SO_3$•pyr., $NEt_3$, DMSO, $CH_2Cl_2$, 0 °C; (g) SEMCl, TBAI, DIPEA, $CH_2Cl_2$, 40 °C; 86% (2 steps); (h) KHMDS, TMSCl, $NEt_3$, THF, –78 °C; (i) NBS, THF, 0 °C; 65% (2 steps).

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[75] Sanz, R.; Castroviejo, M. P.; Fernández, Y.; Fañanás, F. J. *J. Org. Chem.* **2005**, *70*, 6548-6551.

[76] Sibi, M. P.; Snieckus, V. *J. Org. Chem.* **1983**, *48*, 1935-1937.

[77] Glennon, R. A.; Raghupathi, R.; Bartyzel, P.; Teitler, M.; Leonhardt, S. *J. Med. Chem.* **1992**, *35*, 734-740.

[78] Rawat, M.; Prutyanov, V.; Wulff, W. D. *J. Am. Chem. Soc.* **2006**, *128*, 11044-11053.

Intermediate **2.13** was then carried forward two additional steps via benzyl protection of the phenol and a one-pot conversion to the TMS-protected alkyne **2.14**. These steps also did not require chromatography as simple trituration and crystallization yielded pure material. Protected alkyne **2.14** was then lithiated and coupled via a Felkin-selective process to **2.17**, a known ketone[79] derived from lactic acid, to produce **2.15** in 6:1 dr after deprotection. This diastereomer ratio was improved to >98:2 upon recrystallization, and the major diastereomer was determined via X-ray crystallography (Figure 2.2). Four subsequent steps were then carried out to produce bromoketone **2.9**.

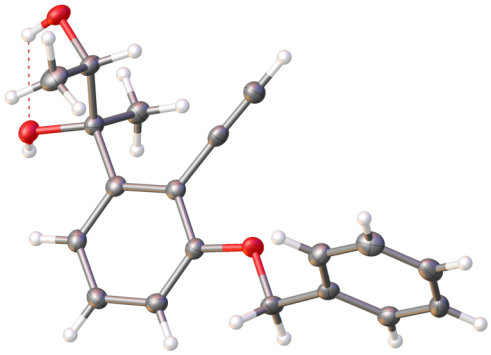

**Figure 2.2** X-ray crystal structure of diol **2.15** confirms the stereochemistry of the C6-tertiary carbinol.[80]

The synthesis of the eastern fragment commenced with the two-step conversion of Garner's aldehyde **2.18**[81] to alkynoate **2.19** (Scheme 2.4).[82,83] A completely regioselective

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[79] Overman, L. E.; Rishton, G. M.; *Org. Synth.* Coll. Vol. 9, 139; Ann. Vol. 71, 56.

[80] This image was generated by Shao-Liang Zheng from the Harvard University X-ray Crystallographic Laboratory.

[81] Garner, P.; Park, J. M. *Org. Synth*. Coll. Vol. 9, 300; Ann. Vol. 70, 18.

[82] Mander, L. N.; Sethi, S. P. *Tet. Lett.* **1983**, *48*, 5425-5428.

[83] (a) Ohira, S. *Synth. Comm.* **1989**, 19, 561-564. (b) Müller, S.; Liepold, B.; Roth, G. J.; Bestmann, H.-J. *Synlett*. **1996**, 521-522.

nitrile-oxide cycloaddition was then performed[84] yielding benzyloxy-isoxazole **2.20**.[85] Asymmetric allylation,[86] protecting group manipulation, and Dess-Martin oxidation[87] yielded aldehyde **2.23**. While each of the reactions in this sequence was scalable, the final oxidation was the most challenging to perform on large scale. Specifically, oxidation of primary alcohol **2.22** proceeds cleanly and rapidly as observed in NMR tube experiments. However, extraction of the aldehyde from the reaction mixture required significant optimization since **2.23** is exceedingly sensitive to basic conditions, and also decomposes readily upon sustained heating (during solvent evaporation for example). Thus, quenching of the reaction required the use of pH 7 buffer and rotory evaporation necessitated a bath temperature of < 30 °C.

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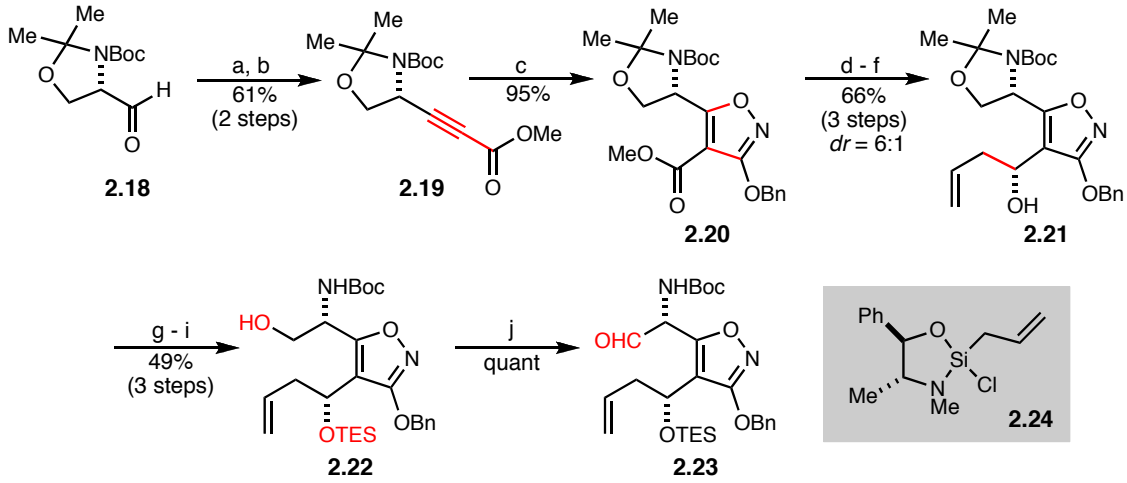
[84] El-Seedi, H. R.; Jensen, H. M.; Kure, N.; Thomsen, I.; Torssell, K. B. G. *Act. Chem. Scand.* **1993**, *47*, 1004-1011.

[85] Stork, G.; Hagedorn III, A. A. *J. Am. Chem. Soc.* **1978**, *100*, 3609-3611.

[86] Kinnaird, J. W. A; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920-7921.

[87] Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155-4156.

**Scheme 2.4** Synthesis of the eastern fragment **2.23**.




Reagents and conditions: (a) Ohira-Bestmann reagent, $K_2CO_3$, MeOH, 0 °C to rt; (b) *n*-BuLi, $NCCO_2Me$, THF, –78 °C; 61% (2 steps); (c) BnOCHNOH, $KHCO_3$, NCS, EtOAc, 48 °C; 95%; (d) DIBAl-H, toluene, –78 °C; (e) $SO_3$•pyr., $NEt_3$, DMSO, $CH_2Cl_2$, 0 °C; (f) Leighton reagent **2.24** (1st gen.), toluene, –10 °C; 66%, *dr* = 6:1 (3 steps); (g) TFA, MeOH, 0 °C; $Boc_2O$, $NaHCO_3$, dioxane, 0 °C; (h) TESCl, Imidazole, DMF, rt; (i) AcOH, MeOH, 0 °C to rt; 49% (3 steps); (j) DMP, $CH_2Cl_2$, rt; quantitative.

The Stork-Hagedorn benzyloxy-isoxazole[49] has been a mainstay in modern tetracycline syntheses since it masks the difficult-to-handle vinylogous carbamic acid, and is easy to cleave late-stage (Scheme 2.5). Our strategy for the generation of this heterocycle (Scheme 2.3, **2.19** to **2.20**) was a critical component of the synthesis, and thus deserves comment. At the outset of this work, literature precedent involved the synthesis of an unfunctionalized isoxazole, followed by subsequent elaboration.[48,55,88] This elaboration phase typically requires strong-base deprotonations of weakly activated positions, greatly reducing the functional group tolerability of the approach. Since we targeted Garner's aldehyde as an ideal starting point for the synthesis of **2.23**, this eliminated the applicability of precedent and created a need for an alternative method.

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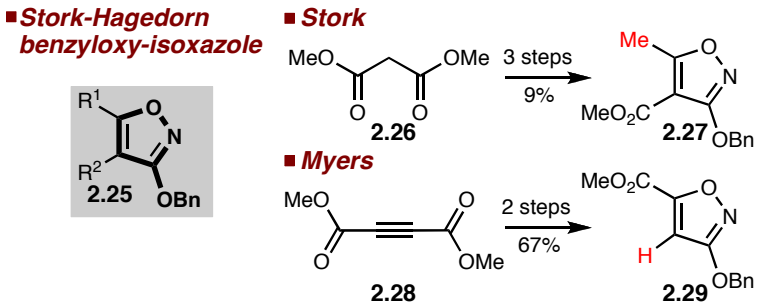
[88] A third method to produce benzyloxy-isoxazolines from the corresponding bromo-isoxazole involves alkoxide displacement, see: Conti, P.; De Amici, M.; Roda, G.; Pinto, A.; Tamborini, L.; Madsen, U.; Nielsen, B.; Bräuner-Osborne, H.; De Micheli, C. *Tetrahedron* **2007**, *63*, 2249-2256.

**Scheme 2.5** Traditional approaches to benzyloxy-isoxazoles. Sites that require functionalization are highlighted in red.[48,49,55]




A literature disclosure by Torssell attracted our attention since it revealed that the seldom-used N-hydroxy benzylformimidate (**2.31**, Scheme 2.6) is a competent nitrile-oxide precursor.[84] Indeed, utilization of this reagent in the context of our synthesis was quite successful (*vide supra*). Yet, we were unable to produce the significant quantity of **2.31** that was needed using the reported procedure. Therefore, we initially attempted to intercept the requisite benzyloxy nitrile-oxide generated in our [3+2] cycloaddition via activation of various O-silylated hydroxamic acids,[89] however these attempts were unsuccessful. Thus, we turned to the development of a new route to **2.31**, ultimately resulting in the execution of a coupling reaction employing the Vilsmeier reagent,[90,91] benzyl alcohol, and hydroxylamine.[92] After extensive optimization, which was required due to the propensity of intermediate **2.33** to decompose forming benzyl chloride and DMF, we

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[89] Muri, D.; Bode, J. W.; Carreira, E. M. *Org. Lett.* **2000**, *2*, 539-541.

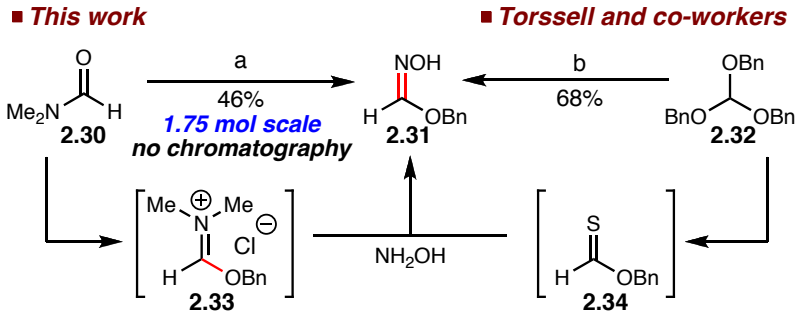
[90] Vilsmeier, A.; Haack, A. *Chem. Ber.* **1927**, *60*, 119-122.

[91] While multiple methods exist for the synthesis of the Vilsmeier reagent, we preferred the procedure reported by Ramage and co-workers, see: Jiang, L.; Davison, A.; Tennant, G.; Ramage, R. *Tetrahedron* **1998**, *54*, 14233-14254.

[92] Conditions for the synthesis of aryl hydroximates are known, see: Tanyama, E.; Imada, S.; Okui, A.; Kin, E. Japanese Patent 05,051,357, March 2, 1993. However, these conditions failed in our hands to yield **2.31**. Further, these conditions required the use of the alcohol nucleophile as co-solvent, a requirement that was not practical for our system.

have been able to synthesize over 120 grams of **2.31** in a single batch via the conditions outlined in Scheme 2.6.

**Scheme 2.6** Comparison of methods to produce **2.31**.




Reagents and conditions: (a) $SOCl_2$; BnOH, DMF, pyr., $H_2NOH{\cdot}HCl$, –40 °C to 0 °C; 46% (b) $H_2S$, $H_2NOH{\cdot}HCl$, NaOH, $K_2CO_3$, rt; 68% (reported).

The coupling of fragments **2.9** and **2.23** proved more difficult than anticipated due to the propensity for the aldehyde to decompose (Scheme 2.7). Accordingly, a mild samarium diiodide-promoted Reformatsky reaction was employed to facilitate an aldol coupling of the two fragments.[93] The aldol adducts were immediately treated with CSA to cleave the TES group, producing **2.35** as a 1:1.2 ratio of diastereomers. At this point, the two C4a-diastereomers were separated, and carried on individually to macrocycle **2.3**. Conversion of the terminal olefin to an oxime was uneventful, yielding **2.36** in a high-yielding three-step procedure for both diastereomers. The nitrile-oxide macrocyclization of intermediate **2.36** proved to be a very efficient reaction for either diastereomer as well. While macrocyclizations of this type have been documented using various conditions,[94,95]

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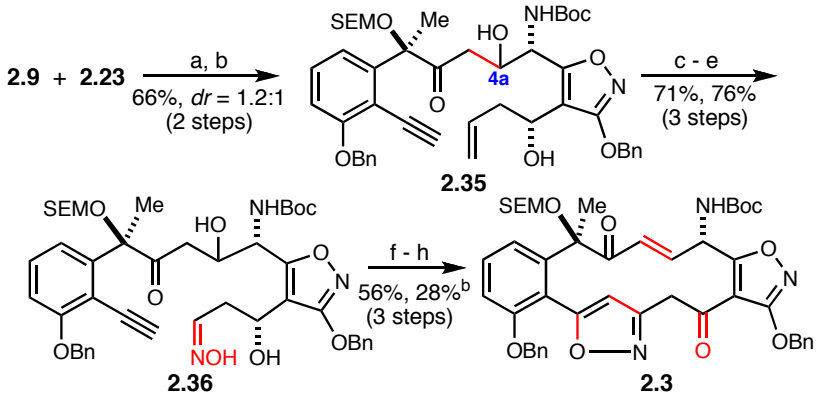
[93] (a) Moslin, R. M.; Jamison, T. F. *J. Am. Chem. Soc.* **2006**, *128*, 15106-15107. (b) Sparling, B. A.; Moslin, R. M.; Jamison, T. F. *Org. Lett.* **2008**, *10*, 1291-1294.

[94] For the preparation of nitrile-oxides from oximes via chlorination see: Liu, K.-C.; Shelton, B. R.; Howe, R. K. *J. Org. Chem.* **1980**, *45*, 3916-3918.

[95] (a) Sengupta, J.; Mukhopadhyay, R.; Bhattacharjya, A.; Bhadbhade, M. M.; Bhosekar, G. V. *J. Org. Chem.* **2005**, *70*, 8579-8582. (b) Paek, S.-M.; Seo, S.-Y.; Kim, S.-H.; Jung, J.-W.; Lee, Y.-S.; Jung, J.-K.;

we found that the conditions developed by Mulzer[96] worked best in our system (NCS, pyridine, refluxing chloroform). Finally, a regioselective dehydration was performed with the Martin sulfurane reagent,[97] followed by oxidation of the remaining alcohol to afford macrocycle **2.3**. Intriguingly, one C4a alcohol diastereomer underwent dehydration at higher temperature, highlighting the reduced reactivity of functionalities that are presumably placed on the interior of a macrocycle. With this key compound in hand, we were able to explore the transannular reactions proposed in the planning stage of the synthesis.

**Scheme 2.7** Fragment coupling and elaboration.




Reagents and conditions: (a) $SmI_2$, THF, –78 °C; (b) CSA, MeOH, $CH_2Cl_2$, 0 °C; 66% (2 steps); (c) 5 mol% $OsO_4$, NMO, acetone, THF, pH 7 phosphate buffer, rt; (d) $NaIO_4$, THF, pH 7 phosphate buffer, rt; (e) $NH_2OH{\cdot}HCl$, pyridine, EtOH, rt; 71%, 76% (3 steps);[a] (f) NCS, pyridine, $CHCl_3$, 60 °C; (g) Martin sulfurane, $CH_2Cl_2$, –78 °C to –55 °C; (h) DMP, $NaHCO_3$, $CH_2Cl_2$; 56%, 14% (28% brsm), (3 steps).[a] [a] Consecutive yields refer to the yield for each C4a diastereomer.

## III. Macrocyclic Stereocontrol

The first transformation that was attempted with macrocycle **2.3** was a transannular Michael addition; this addition should establish both the A-ring of the tetracycline core as

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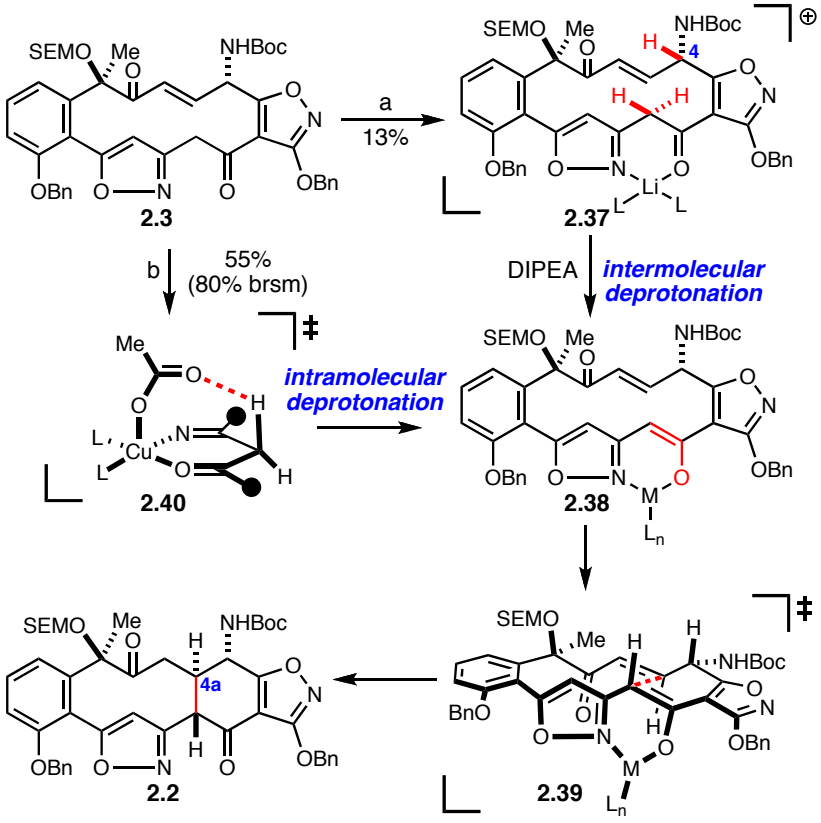
Suh, Y.-G. *Org. Lett.* **2005**, *7*, 3159-3162. (c) Paek, S.-M.; Yun, H.; Kim, N.-J.; Jung, J.-W.; Chang, D.-J.; Lee, S.; Yoo, J.; Park, H.-J.; Suh, Y.-G. *J. Org. Chem.* **2009**, *74*, 554-561.

[96] Enev, V. S.; Drescher, M.; Mulzer, J.; *Tetrahedron* **2007**, *63*, 5930-5939.

well as the C4a-tertiary stereogenic center. Initial experiments indicated that few metal ions were competent in the execution of the desired transformation. However, soft-enolization conditions employing the use of lithium bromide and DIPEA did afford the desired product **2.2** in 13% yield and as a single diastereomer (Scheme 2.8). Disappointingly, the major product of this reaction was an enamine consistent with isomerization of the enone moiety into the C4 position (61% yield).

**Scheme 2.8** Two pathways towards enolate **2.38**, and Michael addition to **2.2**.




Reagents and conditions: a) LiBr, DIPEA, EtOAC, rt; 13%; (b) $Cu(OAc)_2 \cdot H_2O$, MeOH, 0 °C; 55% (80% brsm).

The poor yield of **2.2** obtained with lithium bromide and DIPEA suggested that a new enolization strategy was required. It was hypothesized that upon lithium-ion com-

[97] Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5003-5010.

plexation, activation of hydrogen atoms at both the C12a and C4 positions may occur simultaneously. Since the deprotonation is presumably an intermolecular process, the enhanced acidity at both positions led to an unselective mixture of deprotonated intermediates. In an effort to overcome this problem, we considered the use of metal-ions containing basic ligands since a selective intramolecular deprotonation could occur under this scenario. Accordingly, various metal acetates were screened for reactivity, allowing us to identify $Cu(OAc)_2 \cdot H_2O$ as a competent reagent to effect this transformation. In the first key step of the synthesis we were able to obtain **2.2** in 55% yield (80% brsm) and as a single diastereomer.[98] Despite the facile nature of this transformation, the reaction was stopped prior to complete conversion due to an emerging byproduct that forms from oxidation of the Michael product with Cu(II).[99] The stereochemistry was determined via 1D nOe data and coupling constants, and all data obtained for this product are consistent with the proposed structure.

---

[98] $Cu(OAc)_2 \cdot H_2O$ has been shown to facilitate deprotonations in somewhat related nitro-aldol (Henry) reactions, see: Evans, D. A.; Seidel, D.; Rueping, M.; Lam, H. W.; Shaw, J. T.; Downey, C. W. *J. Am. Chem. Soc.* **2003**, *125*, 12692-12693.

[99] (a) Baran, P. S.; Richter, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 7450-7451. (b) DeMartino, M. P.; Chen, K.; Baran, P. S. *J. Am. Chem. Soc.* **2008**, *130*, 11546-11560.

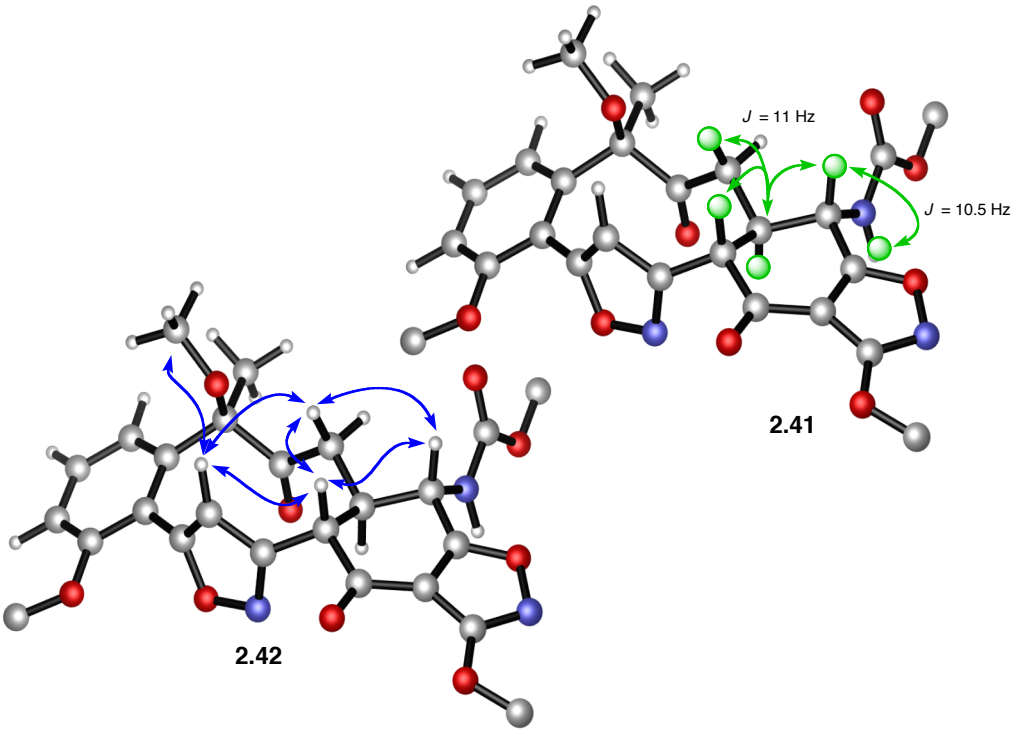



**Figure 2.3** Relevant coupling constant (green arrows, **2.41**) and nOe (blue arrows, **2.42**) and data used to determine the stereochemistry of Michael product **2.2**. Molecular modeling was performed with truncated protecting groups, see reference [100] for details.

### IV. Hydroxylation at C12a

With efficient access to Michael product **2.2**, we turned our attention to what would become the most challenging aspect of this synthesis, hydroxylation at C12a. Our plan for the execution of this transformation was quite similar to our plan to execute the Michael reaction, that is, we intended to perform a soft-enolization at C12a via Lewis acid activation and allow it to react with an electrophilic partner. What was immediately encountered, however, was a strong preference to deprotonate at the C4-position rather than at

---

[100] Molecular modeling of intermediates **2.41**, **2.42**, **2.46**, and **2.47** was performed using Spartan 2008, v. 1.1.2 (Wavefunction, Inc., Irvine, CA, USA), at the molecular mechanics (MM2) level of theory.

C12a (Figure 2.4). We therefore could not access the C12a-hydroxylated product under a variety of conditions, including strong-base deprotonation with LDA or KHMDS.

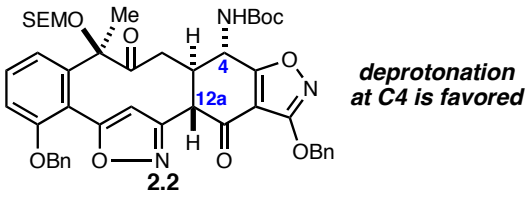
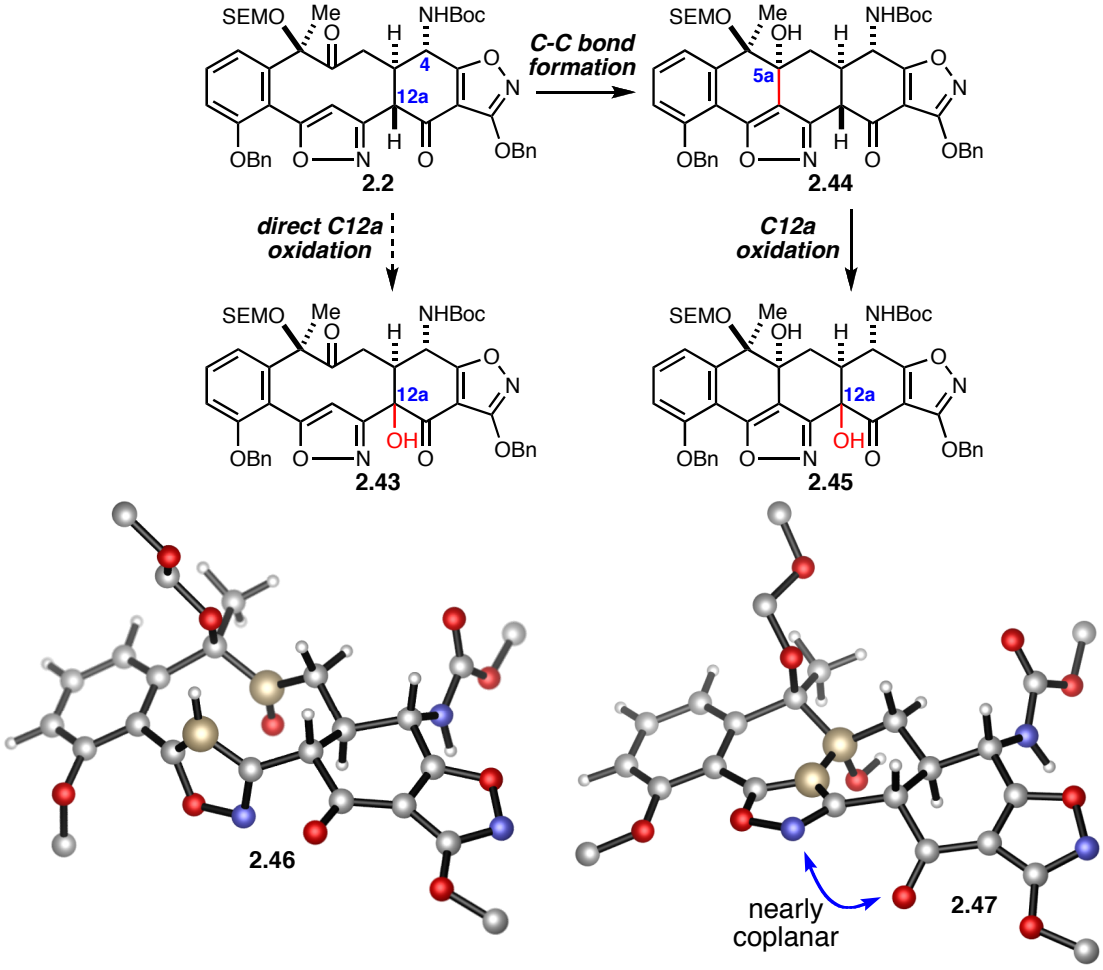



**Figure 2.4** Possible sites for deprotonation under soft-enolization conditions.

Simple molecular modeling[100] of Michael product **2.2** provided insight into this troubling transformation and also revealed a possible solution. With the C12a-C4a bond present, as in intermediate **2.2** (Scheme 2.9), the isoxazole is forced to adopt a conformation that alleviates steric compression across the 10-membered macrocycle (conformer **2.46**). This conformation places the two heteroatoms that were proposed to participate in Lewis-acid complexation anti to one another, effectively eliminating the possibility for bidentate chelation. With newfound understanding of the enolization regioselectivity, it was proposed that the original sequence of events be inverted such that isoxazole substitution is performed prior to C12a-hydroxylation. Contraction of the 10-membered ring to the tetracycline core structure **2.44** places the isoxazole and ketone at a position of near co-planarity, enabling a more effective soft-enolization (conformer **2.47**).

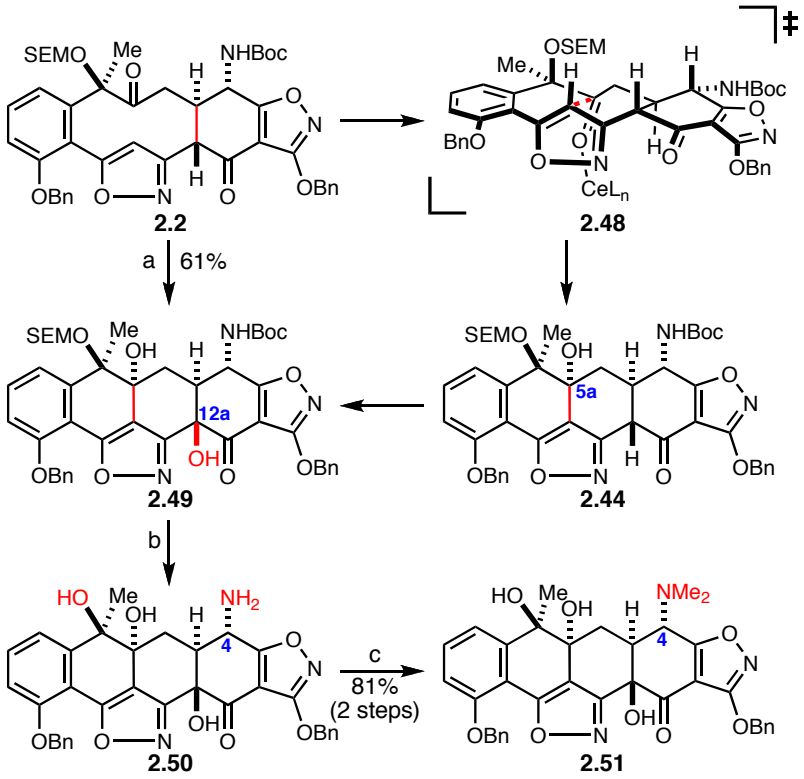
**Scheme 2.9** C12a-hydroxylation requires C-C bond formation prior to oxidation. Gold spheres represent carbon atoms that are required to react in order to achieve an appropriate conformation for hydroxylation. Molecular modeling was performed with truncated protecting groups, see reference [100] for details.




Fortuitously, we discovered a reagent that was capable of carrying out both the isoxazole substitution and C12a-hydroxylation reactions, $CeCl_3 \cdot 7H_2O$ (Scheme 2.10). Treatment of **2.2** with this reagent in an atmosphere of oxygen cleanly furnishes the C12a-oxidized compound **2.49** after reducing the intermediate peroxide with dimethyl

sulfide.[101] The mechanism that accounts for the facile nature of this transformation is most likely an initial Lewis-acid-mediated isoxazole substitution (**2.48**), followed by a cerium-catalyzed hydroxylation reaction.[102,103] Two subsequent transformations were then carried out to deprotect the C6-tertiary carbinol and install the requisite dimethyl amine, thus producing **2.51** in good yield for the entire sequence.

**Scheme 2.10** Conversion of **2.2** to tertiary carbinol **2.51**.




Reagents and conditions: a) $CeCl_3 \cdot 7H_2O$, $O_2$, *i*-PrOH, rt; $Me_2S$, $CH_2Cl_2$, rt; 61%; (b) HCl, THF, rt; (c) $NaBH_3CN$, AcOH, $H_2CO$ (aq.), $CH_3CN$, rt; 81% (2 steps).

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[101] Extended reaction times in the presence of Ce(III) also facilitates reduction of the intermediate peroxide. However, extended stirring with our substrate led to reduced yields; thus we opted to perform the oxidation for a shorter period of time, followed by a second reductive step.

[102] Christoffers, J.; Werner, T. *Synlett*. **2002**, *1*, 119-121.

[103] It is interesting to note that the conditions for this oxidation are similar to those employed by Woodward in the synthesis of (±)-sancycline (see ref. 42 for details). However, in that system the yield was <10%. It is likely that the presence of the C11-C12 isoxazole in our system restricts the number of potential sites for oxidation, improving the overall yield.

Conversion of **2.2** to the C12a-tertiary carbinol **2.49** occurred in a completely stereoselective manner, which in this case was a very unfortunate result given that the stereochemical outcome was exactly opposite to that required to synthesize tetracycline. This result was not unexpected, since attempts to produce a *cis*-ring fusion in similar substrates have been unsuccessful[48] with the exception of the Muxfeldt terramycin synthesis.[44,104] Unfortunately, the lack of reactivity exhibited by 10-membered macrocycle **2.2** demanded that we abandon our initial plan to oxidize prior to ring-contraction, forcing us to seek a solution to the C12a-hydroxylation dilemma with the tetracycline core intact.

In order to more exhaustively probe C12a-hydroxylation, we needed to establish a method to effect the ring contraction of the 10-membered ring in **2.2** without subsequent oxidation at C12a. In other words, we needed to disrupt the cascade after C-C bond formation. This would allow the subsequent exposure of an enolate at C12a to a variety of oxidants. The solution to this problem arose during studies to expand the Michael reaction and cerium-catalyzed reactions into a one-pot procedure. We found that simply mixing both $Cu(OAc)_2 \bullet H_2O$ and $CeCl_3 \bullet 7H_2O$ in methanol afforded the C12a-chlorinated compound **2.53** in a completely diastereoselective and high yielding reaction (Scheme 2.11). Mechanistically, it is believed that the Michael addition occurs first, followed by the isoxazole substitution reaction, and lastly a Cu(II)-mediated[105] chlorination. The methanol adduct arises via trapping of the intermediate oxocarbenium ion after isoxazole

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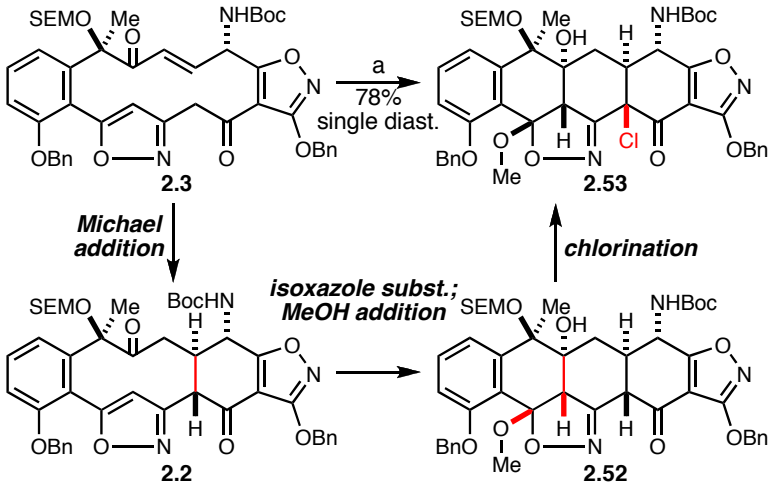
[104] In the Muxfeldt case, we speculate that the acetonide used to protect the C5- and C6-hydroxyl groups gears the molecule in a way that facilitates correct C12a-oxidation. Otherwise, it is unlikely that the reaction would have been successful. See Chapter 3 for further insight into the stereochemical outcome of this reaction.

[105] (a) Giordano, C.; Castaldi, G.; Casagrande, F.; Belli, A. *J. Chem. Soc., Perkin Trans. I* **1982**, 2575-2581. (b) Shi, X.-X.; Dai, L.-X. *J. Org. Chem.* **1993**, *58*, 4596-4598. (c) Nobrega, J. A.; Gonçalves, M. C.; Peppe, C. *Synth. Comm*. **2002**, *24*, 3711-3717.

substitution with methanol from solvent; this was a step that was suppressed in the original hydroxylation procedure since isopropanol was used in that case.

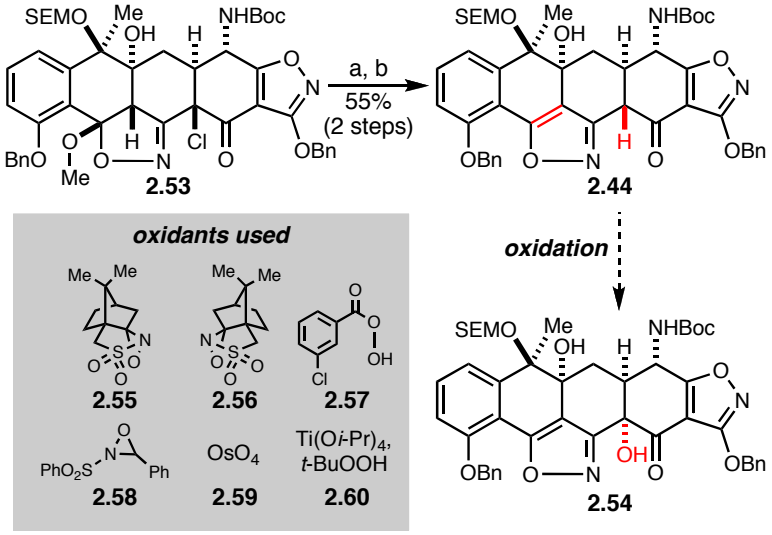
**Scheme 2.11** A transannular cascade producing C12a-chlorinated compound **2.53**.




Reagents and conditions: (a) $Cu(OAc)_2 \cdot H_2O$, $CeCl_3 \cdot 7H_2O$, MeOH, rt; 78%.

With access to intermediate **2.53**, we decided to perform a two-step procedure involving reduction of the C12a-position with samarium diiodide, and restoration of aromaticity to the isoxazole via ejection of methanol under acidic conditions (Scheme 2.12). Intermediate **2.44**, which exists as 5.4:1 mixture of keto:enol tautomers, was then exposed to a variety of oxidants with the hope that the selectivity might be perturbed. Unfortunately, under a variety of conditions, which included both chiral and achiral oxygen-sources, we were unable to obtain any of the desired *cis*-ring fusion. It was at this point in the synthesis, that we decided to re-evaluate our synthesis plan, with the hope that we could arrive at a substrate with a bias toward selective oxidation at C12a with the desired sense of diastereoinduction.

**Scheme 2.12** Attempted synthesis of **2.54**.




Reagents and conditions: (a) $SmI_2$, THF, MeOH, –78 °C; (c) CSA, $CH_2Cl_2$, rt; 55% (2 steps).

## V. Conclusion

This chapter describes the realization of several key objectives as we pursue the synthesis of (–)-tetracycline. First, a route to the targeted macrocycle containing all of the necessary functionality for late-stage manipulation was validated. The synthesis of this macrocycle employed two fragments, each of which was synthesized in an efficient and scalable manner. Secondly, conditions for the execution of a selective transannular Michael addition employing $Cu(OAc)_2 \cdot H_2O$ were discovered, validating the first key step of the synthesis. Further, the complete carbocyclic ring system was synthesized via execution of a second transannular reaction employing $CeCl_3 \cdot 7H_2O$, which additionally facilitated C12a-hydroxylation. While this latter reaction did not yield the appropriate stereochemistry at the C12a-position, the reactivity of the substrate nevertheless was established. Chapter 3 will address the selectivity of this reaction in detail.

# *Chapter 2*

## VI. Experimental Section

### A. General Information

See the "list of abbreviations" section for standard abbreviations of chemicals and protecting groups. Reactions in anhydrous solvents were conducted under an atmosphere of nitrogen or argon in glassware that was flame-dried unless otherwise specified. Analytical thin layer chromatography (TLC) was performed on EMD Reagent 0.25 mm silica gel 60 $F_{254}$ plates. Visualization was accomplished with UV light (254 nm) followed by heating after staining the plate with ceric ammonium molybdate unless otherwise noted. Extraction and chromatography solvents were reagent grade or HPLC grade, and were used without further purification. Product purification was performed by flash column chromatography[106] using Sorbent Technologies silica gel (40-63 μm, 230–400 mesh), MPLC using MP Biomedicals silica gel (18-32 μm), and semi-preparative HPLC using a Rainin Dynamax solvent delivery system empoying an Agilent Zorbax RX-SL 21.2 x 250 nm

[106] Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

column and Rainin Dynamax absorbance detector model UV-C operating at 215 nm.

**B. Analytical Information**

Unless otherwise stated, all isolated and characterized compounds were >95% pure as judged by $^1$H NMR spectroscopic analysis. $^1$H NMR spectra were recorded at room temperature on a Varian Inova 600 spectrometer (600 MHz), a Varian Inova 500 spectrometer (500 MHz), or a Mercury 400 spectrometer (400 MHz). $^1$H NMR data are reported in the following format: chemical shift (multiplicity, coupling constants, integration). Chemical shifts are reported in ppm with the residual solvent resonance as internal standard (7.26 ppm for $CDCl_3$, 7.15 ppm for $C_6D_6$, 2.05 ppm for acetone-$d_6$, 3.58 ppm for THF-$d_8$, and 2.49 ppm for DMSO-$d_6$). Multiplicity is abbreviated as follows: m = multiplet, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, oct = octet, br = broad, app = apparent.

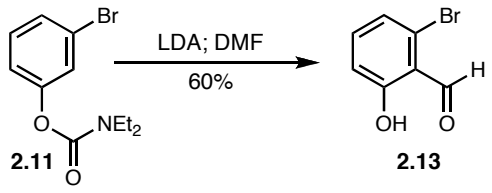
$^{13}$C NMR spectra were recorded at room temperature on a Varian Inova 500 spectrometer (126 MHz), or a Mercury 400 spectrometer (101 MHz) with broadband proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as internal standard (77.0 ppm for $CDCl_3$, 128.0 ppm for $C_6D_6$, 206.0 ppm for acetone-$d_6$, 67.4 ppm for THF-$d_8$, and 29.5 ppm for DMSO-$d_6$).

Infrared spectra were recorded as thin films on NaCl plates using a Perkin Elmer 1600 series FT-IR spectrometer at a resolution of 4 cm$^{-1}$. Optical rotations were measured on a Jasco P-2000 digital polarimeter with a sodium lamp, and are reported as: $[\alpha]_{T(C)D}$ XX° (*c* (g/100 mL), solvent). High-resolution mass spectra were obtained on an Agilent 6210 TOF LC/MS at the Harvard University Mass Spectrometry Laboratory.

## C. Materials

Tetrahydrofuran, diethyl ether, toluene and dichloromethane employed as reaction solvents were dried by passage through a column of activated alumina under an argon atmosphere.[107] Other reaction solvents (e.g. benzene, acetonitrile, HMPA, etc.) were distilled from calcium hydride under a nitrogen atmosphere prior to use, with the exception of methanol, which was distilled from magnesium prior to use. Amine bases (triethylamine, diisopropylethylamine, diisopropylamine, pyridine) were distilled from calcium hydride prior to use. EMD chloroform stabilized with ethanol, EMD DriSolv dimethyl sulfoxide, and EMD DriSolv *N,N*-dimethylformamide were used.

## D. Experimental Procedures




**2-bromo-6-hydroxybenzaldehyde (2.13).** A flame-dried 5 L 3-necked flask equipped with a mechanical stirrer under an atmosphere of argon was charged with anhydrous THF (735 mL, 1.00 M wrt **2.11**) and cooled to 0 °C. Next, diisopropylamine (124 mL, 0.882 mol, 1.20 equiv.) was added rapidly via syringe, followed by the addition of *n*-BuLi (310 mL of a 2.61 M solution in hexane, 0.809 mol, 1.10 equiv.) over 15 minutes while keeping the internal temperature at ca. 10 °C. This solution was stirred for 15 additional minutes.

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[107] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*. **1996**, *15*, 1518.

Meanwhile, in a 1 L flame-dried flask under argon, **2.11** (200 g, 0.735 mol, 1.00 equiv.) was added followed by the addition of anhydrous THF. Both flasks were then cooled to –78 °C, and **2.11** in THF was added via cannula to the LDA solution over 25 minutes while keeping the internal temperature of the reaction < –72 °C. During this addition, the reaction became dark brown. The reaction was then stirred at –78 °C for an additional 35 minutes. Next, DMF (140 mL, 1.84 mol, 2.50 equiv.) at room temperature was added via syringe directly into the solution over 10 minutes while keeping the internal temperature of the solution < –68 °C. No major color change was noted during this addition. The resulting solution was stirred for 1.25 h at –78 °C, upon which time the cooling bath was removed, revealing a dark green solution. The reaction was stirred for 1.5 h during which time the reaction apppeared red in color. After the reaction reached 5 °C, the solution was transferred via cannula to an Erlenmeyer flask containing 3.5 L of 1.5 *N* HCl at 0 °C over 30 minutes. Bubbling was observed during this addition. After complete transfer, the ice bath was removed and the reaction was stirred for 14 h. The resulting orange/yellow mixture was extracted four times with 750 mL of hexanes each. The organic extracts were then washed two times with 1 L of water each, and then dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude material was purified via flash chromatography on silica gel (25:1 hexanes:EtOAc) affording **2.13** (88.0 g, 60%) as a slightly yellow solid. The physical data of **2.13** was in agreement with the data reported in the literature.[108]

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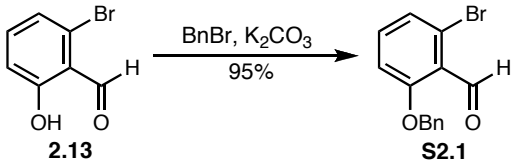
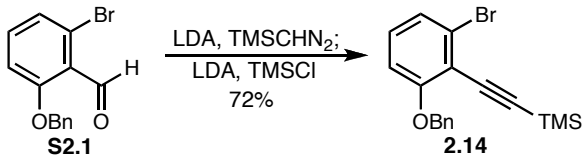
[108] Rawat, M.; Prutyanov, V.; Wulff, W. D. *J. Am. Chem. Soc.* **2006**, 128, 11044.

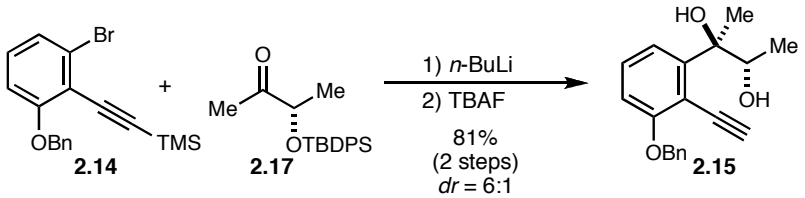



**2-(benzyloxy)-6-bromobenzaldehyde (S2.1).** To a solution of **2.13** (88.0 g, 0.438 mol, 1.00 equiv.) exposed to air in DMF (550 mL, 0.8 M) at room temperature, $K_2CO_3$ (63.6 g, 0.460 mol, 1.05 equiv.) was added in a single portion, followed by the rapid addition of BnBr (53.1 mL, 0.447 mol, 1.02 equiv.) via syringe. The reaction was then capped and stirred for 14 h, upon which time the reaction was poured into a separatory funnel containing 1 L of water (caution, slightly exothermic). The mixture was extracted three times with 750 mL of $Et_2O$ each, and the aqueous extracts were washed one time with brine. The resulting solution was dried with $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified via triteration in hexanes at room temperature affording **S2.1** (121 g, 95%) as a white solid. $\boldsymbol{R_f}$ = 0.73 (6:1 hexanes:EtOAc); **MP** = 54-56°C; **IR** (neat) 3090, 3030, 2879, 1745, 1691, 1583, 1567, 1444, 1411, 1390, 1286, 1178, 1021, 879, 834; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.47 – 7.23 (m, 7H), 7.00 (dd, $J$ = 8.0, 1.2 Hz, 1H), 5.19 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 189.97, 161.09, 135.61, 134.58, 128.66, 128.20, 127.02, 126.80, 124.16, 123.88, 112.44, 70.87; **HRMS**: Exact mass calcd for $C_{14}H_{11}BrO_2$ [(M+$Na^+$)]: 312.9835; found: 312.9831 (ESI).




**((2-(benzyloxy)-6-bromophenyl)ethynyl)trimethylsilane (2.14).** A flame-dried 3-necked 3 L flask equipped with a mechanical stirrer under an atmosphere of argon was charged with THF (630 mL, 0.3 M), followed by addition of diisopropylamine (30.6 mL, 0.219 mol, 1.15 equiv.) rapidly via syringe. This solution was cooled to 0 °C, and *n*-BuLi (76.4 mL of a 2.61 M solution in hexane, 0.200 mol, 1.05 equiv.) was added rapidly while keeping the internal temperature of the solution < 10 °C. After stirring for 20 minutes, the solution was cooled to –78 °C and $TMSCHN_2$ (100 mL of a 2.0 M solution in hexane, 0.200 mol, 1.05 equiv.) was added rapidly directly into the solution via syringe while keeping the internal temperature < –68 °C. The reaction was allowed to stir for 30 minutes at –78 °C, upon which time **S2.1** (55.5 g, 190 mmol, 1.00 equiv.) in THF (380 mL, 0.5 M) at –78 °C under an atmosphere of nitrogen was added to the reaction mixture directly into the solution via cannula over 15 minutes. The resulting slightly orange solution was stirred for 10 minutes at –78 °C, upon which time it was warmed to room temperature by removal of the cooling bath. The reaction was stirred for 3 h, during which time the solution turned red/orange and slow bubbling was observed. During this warming period, a second solution of LDA was prepared via addition of *n*-BuLi (76.4 mL of a 2.61 M solution in hexane, 0.200 mol, 1.05 equiv.) to diisopropylamine (30.6 mL, 0.219 mmol, 1.15 equiv.) in THF (380 mL, 0.5 M wrt **S2**) at 0 °C. Upon completion of the 3-hour warming period, the reaction mixture was cooled back to –78 °C, and the newly prepared LDA solution (also at –78 °C) was added via cannula over 15 minutes directly into the

solution. The cloudy and intensely red solution was stirred at –78 °C for 25 minutes, upon which time TMSCl (60.7 mL, 0.475 mol, 2.50 equiv.) at room temperature was added along the side of the flask via cannula over 10 minutes. The resulting clear red solution was stirred for 20 minutes at –78 °C, upon which time the reaction was quenched with 500 mL of sat. $NaHCO_3$, and warmed to room temperature. The resulting cloudy yellow mixture was diluted with water (2 L) and the resulting mixture was extracted three times with $Et_2O$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified via crystallization from hexanes (250 mL, heated to reflux and gently cooled to 0 °C) affording **2.14** (49.0 g, 72%) as a slightly yellow solid. $\boldsymbol{R_f}$ = 0.50 (10:1 hexanes:EtOAc); **MP** = 71-73°C; **IR** (neat) 2959, 2899, 2160, 1584, 1561, 1450, 1440, 1282, 1265, 1250, 1026, 863, 844; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.9, 1.0 Hz, 2H), 7.38 (dd, *J* = 10.2, 4.7 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.19 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.09 (t, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 5.15 (s, 2H), 0.28 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 160.83, 136.53, 129.72, 128.42, 127.79, 126.85, 126.72, 124.87, 115.84, 111.20, 104.39, 99.25, 70.61, -0.09; **HRMS**: Exact mass calcd for $C_{18}H_{19}BrOSi$ [$(M+Na^+)$]: 381.0281; found: 381.0284 (ESI).

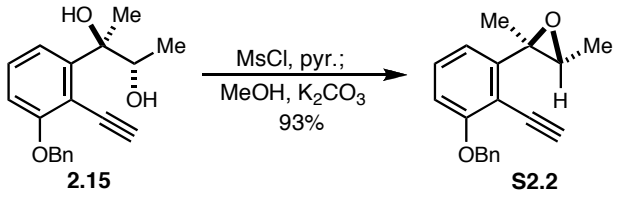



**(*2R,3S*)-2-(3-(benzyloxy)-2-ethynylphenyl)butane-2,3-diol (2.15).** To a solution of **2.14** (18.8 g, 52.3 mmol, 1.00 equiv.) in THF (174 mL, 0.3 M) at –78 °C under an atmos-

phere of nitrogen, *n*-BuLi (20.6 mL of a 2.66 M solution in hexane, 1.05 equiv.) was added over 5 minutes directly into the solution while keeping the internal temperatures < –70 °C. The reaction was allowed to stir for 25 minutes, upon which time **2.17** (17.1 g, 52.3 mmol, 1.00 equiv.) in THF (174 mL, 0.3 M) at room temperature was added via cannula directly into the reaction mixture over 25 minutes. During this addition the internal temperature was kept < –68 °C. The resulting yellow solution was stirred at –78 °C for 50 minutes, upon which time it was quenched with sat. $NH_4Cl$ (100 mL) at –78 °C and allowed to warm to room temperature. Upon warming, the reaction was poured into an Erlenmeyer flask containing 400 mL of $H_2O$, and stirred vigorously for 5 minutes. The resulting mixture was extracted three times with $Et_2O$, the combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. $\boldsymbol{R_f}$ = 0.64 (6:1 hexanes:EtOAc)

The crude residue was dissolved in THF (174 mL, 0.3 M wrt **2.14**) and cooled to 0 °C under an atmosphere of nitrogen. To this solution, TBAF (160 mL of a 1.0 M in THF, 3.00 equiv.) was added directly to the solution via syringe over 5 minutes. The reaction was allowed to stir for 14 h, during which the ice bath was allowed to slowly expire. The reaction was quenched at room temperature (with a water bath present to dissipate any potential heat) with sat. $NH_4Cl$ (100 mL), and stirred for 5 minutes. The mixture was then diluted with 300 mL of $H_2O$ and extracted three times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified via flash chromatography on silica gel (2:1 hexanes:EtOAc) affording **2.15** as a 6:1 ratio of diastereomers (12.6 g, 81%). The undesired diastereomer was removed via recrystallization from 100 mL of a 1:1 mixture of hexanes:EtOAc to obtain material with < 5% undesired diastereomer as determined via NMR. $\boldsymbol{R_f}$ = 0.28 (2:1 hex-

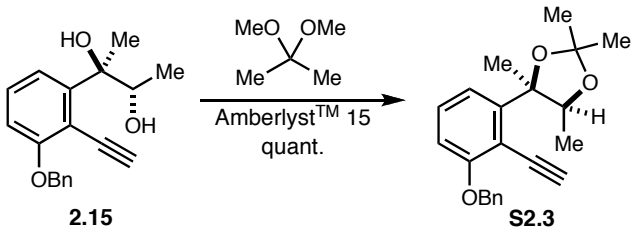
anes:EtOAc); **MP** = 126-128°C; $[\alpha]_D$ = –17 (*c* 0.45, $CHCl_3$); **IR** (neat) 3413, 3286, 2879, 2360, 1572, 1443, 1372, 1265, 1027, 742; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.35 – 7.27 (m, 3H), 6.87 (d, *J* = 8.1 Hz, 1H), 5.17 (s, 2H), 4.87 – 4.72 (m, 1H), 3.69 (s, 1H), 2.93 (s, 1H), 1.81 (s, 3H), 0.99 (d, *J* = 6.4 Hz, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 161.30, 149.58, 136.78, 129.64, 128.49, 127.78, 126.84, 118.67, 111.07, 108.12, 88.54, 79.58, 77.34, 70.96, 70.57, 25.13, 17.75; Mass unable to be obtained under the specified ionization conditions (ESI).




**2.15** **S2.2**

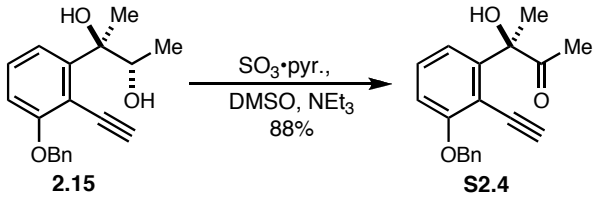
**(*2R,3R*)-2-(3-(benzyloxy)-2-ethynylphenyl)-2,3-dimethyloxirane (S2.2).** To a solution of **2.15** (105 mg, 0.354 mmol, 1.00 equiv.) in $CH_2Cl_2$ (1.18 mL, 0.3 M) at room temperature under an atmosphere of nitrogen, pyridine (0.43 mL, 5.31 mmol, 15 equiv.) was added, followed by the addition of MsCl (44 μL, 0.566 mmol, 1.6 equiv.) dropwise directly into the solution. The reaction was stirred at room temperature for 1 hour, upon which time the flask was sealed and heated to 40 °C for 1 hour. The flask was cooled to room temperature, and methanol (5 mL) was added, followed by $K_2CO_3$ (490 mg, 3.54 mmol, 10 equiv.). The resulting suspension was stirred for 1.5 h at room temperature, upon which time the reaction was poured into a sep. funnel, diluted with $H_2O$ and extracted with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified via flash chromatography on silica gel (10:1

hexanes:EtOAc) affording **S2.2** (92 mg, 93%) as a colorless oil. $R_f$ = 0.76 (3:1 hexanes:EtOAc); $[\alpha]_D$ = –74 (*c* 0.55, $CHCl_3$); **IR** (neat) 3283, 2996, 1574, 1450, 1380, 1298, 1264, 1028, 876, 793, 740, 696, 612; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.0 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.06 (dd, *J* = 7.7, 1.0 Hz, 1H), 6.82 (dd, *J* = 8.4, 0.8 Hz, 1H), 5.18 (s, 2H), 3.56 (s, 1H), 3.10 (q, *J* = 5.5 Hz, 1H), 1.60 (s, 3H), 1.46 (d, *J* = 5.5 Hz, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 159.98, 149.09, 136.99, 130.19, 128.77, 128.06, 127.11, 118.87, 111.46, 109.86, 86.37, 78.53, 70.69, 62.19, 60.51, 18.45, 14.46; **HRMS**: Exact mass calcd for $C_{19}H_{18}O_2$ [(M+$Na^+$)]: 301.1199; found: 301.1194 (ESI).



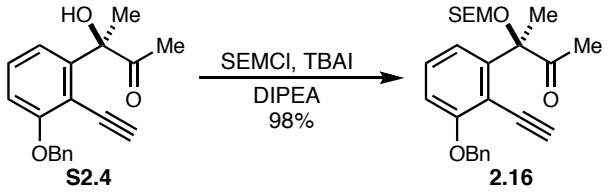

**(*4R,5S*)-4-(3-(benzyloxy)-2-ethynylphenyl)-2,2,4,5-tetramethyl-1,3-dioxolane (S2.3).** To a solution of **2.15** (114 mg, 0.385 mmol, 1.00 equiv.) in $CH_2Cl_2$ (1.3 mL, 0.3 M) at room temperature under an atmosphere of nitrogen, dimethyoxypropane (142μL, 1.16 mmol, 3 equiv.) was added, followed by 15 mg of Amberlyst™ 15 beads. The reaction was stirred for 1 hour, upon which time the solution was filtered through a plug of cotton and concentrated *in vacuo*. The residue was purified via flash chromatography on silica gel (10:1 hexanes:EtOAc) affording **S2.3** (129 mg, quant.) as a colorless oil. $R_f$ = 0.73 (3:1 hexanes:EtOAc); $[\alpha]_D$ = –106 (*c* 0.55, $CHCl_3$); **IR** (neat) 3283, 2984, 2937,

1574, 1448, 1371, 1290, 1263, 1234, 1098, 1047, 1028, 743, 696; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.44 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.24 (m, 2H), 6.86 (dd, *J* = 8.3, 0.7 Hz, 1H), 5.17 (s, 2H), 4.84 (q, *J* = 6.5 Hz, 1H), 3.59 (s, 1H), 1.86 (s, 1H), 1.55 (s, 3H), 1.51 (s, 3H), 1.06 (d, *J* = 6.5 Hz, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 161.06, 149.76, 137.09, 129.78, 128.73, 128.01, 127.10, 119.20, 111.33, 108.81, 108.49, 87.71, 86.64, 80.45, 79.92, 70.81, 30.38, 29.62, 28.21, 19.53; **HRMS**: Exact mass calcd for $C_{22}H_{24}O_3$ [$(M+H^+)$]: 337.1798; found: 337.1814 (ESI).




***(R)*-3-(3-(benzyloxy)-2-ethynylphenyl)-3-hydroxybutan-2-one (S2.4).** To a solution of **2.15** (4.60 g, 15.5 mmol, 1.00 equiv.) in $CH_2Cl_2$ (52 mL, 0.3 M) at 0 °C under an atmosphere of nitrogen, DMSO (9 mL, 1.7 M) was added followed by triethylamine (8.64 mL, 62.0 mmol, 4.00 equiv.). To a second flask, DMSO (23 mL, 2 M wrt $SO_3$•pyr.) was added, followed by $SO_3$•pyr. (7.40 g, 46.5 mmol, 3 equiv.). This mixture was stirred for 5 minutes upon which time most solid had dissolved. Next, the $SO_3$•pyr. solution was added to the solution containing **2.15** over 3 minutes via syringe. The resulting clear and slightly brown mixture was stirred for 1.25 h at 0 °C, upon which time the reaction was poured directly onto a silica gel column and purified via flash chromatography (3:1 hexanes:EtOAc) affording **S2.4** (4.02 g, 88%) as a colorless liquid. $\boldsymbol{R_f}$ = 0.25 (3:1 hex-

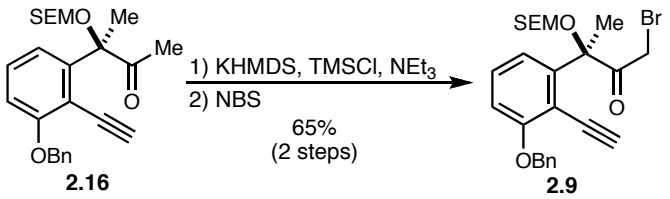
anes:EtOAc); $[\alpha]_D$ = –36 (*c* 0.95, $CHCl_3$); **IR** (neat) 3467, 3280, 1717, 1573, 1451, 1354, 1271, 1128, 1027, 790, 742, 697, 616; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 5.18 (s, 2H), 4.49 (s, 1H), 3.56 (s, 1H), 2.12 (s, 3H), 1.75 (s, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 208.87, 161.21, 145.37, 136.51, 129.76, 128.48, 127.80, 126.79, 118.90, 112.56, 110.45, 89.10, 80.00, 77.58, 70.57, 24.68, 24.47; **HRMS**: Exact mass calcd for $C_{19}H_{18}O_3$ [$(M+H^+)$]: 295.1329; found: 295.1335 (ESI).



**S2.4** **2.16**

***(R)*-3-(3-(benzyloxy)-2-ethynylphenyl)-3-((2-(trimethylsilyl)ethoxy)methoxy)butan-2-one (2.16).** To a solution of **S2.4** (924 mg, 3.14 mmol, 1.00 equiv.) in $CH_2Cl_2$ (3.1 mL, 1.0 M) at room temperature under an atmosphere of nitrogen, DIPEA (2.19 mL, 12.6 mmol, 4.00 equiv.) was added followed by SEMCl (1.67 mL, 9.42 mmol, 3.00 equiv.) rapidly directly into the solution. Next, TBAI (1.16 g, 3.14 mmol, 1.00 equiv.) was added, the reaction was sealed and heated to 40 °C. The reaction was stirred at this temperature for 20 h, upon which time the brown mixture was quenched with sat. $NH_4Cl$ (10 mL), diluted with $H_2O$ (10 mL), and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated. The crude residue was purified via flash chromatography on silica gel (8:1 hexanes:EtOAc) affording **2.16** (1.30 g, 98%) as a colorless liquid. $R_f$ = 0.76 (2:1 hexanes:EtOAc); $[\alpha]_D$ = –39 (*c* 1.2, $CHCl_3$); **IR**

(neat) 3281, 2952, 2894, 1721, 1574, 1449, 1351, 1274, 1249, 1023, 860, 836, 742, 696; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.35 (dt, *J* = 19.8, 7.2 Hz, 5H), 6.93 (d, *J* = 7.2 Hz, 1H), 5.17 (s, 2H), 4.73 (dd, *J* = 23.6, 7.2 Hz, 2H), 3.67 (qd, *J* = 17.3, 9.2 Hz, 2H), 3.53 (s, 1H), 2.21 (s, 3H), 1.76 (s, 3H), 1.00 – 0.77 (m, 2H), 0.01 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 206.57, 160.91, 146.03, 136.66, 129.60, 128.50, 127.80, 126.83, 119.04, 112.05, 109.86, 90.09, 89.20, 84.32, 77.67, 70.54, 65.75, 25.80, 21.06, 18.01, -1.42; **HRMS**: Exact mass calcd for $C_{25}H_{32}O_4Si$ [$(M+H^+)$]: 425.2143; found: 425.2140 (ESI).

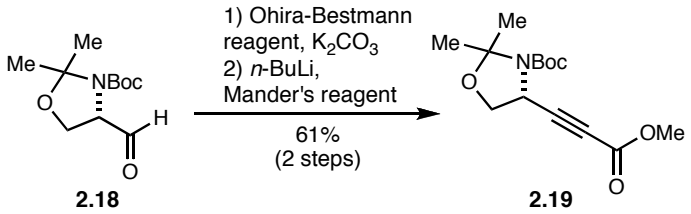



***(R)*-3-(3-(benzyloxy)-2-ethynylphenyl)-1-bromo-3-((2-(trimethylsilyl)ethoxy)methoxy)-butan-2-one (2.9).** To a solution of **2.16** (1.51 g, 3.56 mmol, 1.00 equiv.) in THF (18 mL, 0.2 M) at –78 °C under an atmosphere of nitrogen, a solution of KHMDS (781 mg, 3.92 mmol, 1.10 equiv.) in THF (18 mL THF, 0.1 M wrt **10**) at room temperature was added via syringe over 3 minutes. The resulting slightly yellow solution was stirred for 30 minutes at –78 °C, upon which time TMSCl (2.26 mL, 17.8 mmol, 5.00 equiv.) was added directly into the solution. The yellow color faded after this addition, and the resulting solution was stirred at –78 °C for 15 minutes, upon which time triethylamine (2.98 mL, 21.4 mmol, 6.00 equiv.) was added and the reaction was stirred for another 15 minutes. Next, the reaction was quenched with sat. $NaHCO_3$ and warmed to room temperature and the resulting mixture was extracted three times with $Et_2O$. The

perature and the resulting mixture was extracted three times with $Et_2O$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified via flash chromatography on silica gel (10:1 hexanes:EtOAc with 0.5% triethylamine) affording an intermediate silyl enol ether (1.32 g, 75%). $R_f$ = 0.59 (6:1 hexanes:EtOAc).

The silyl enol ether (1.32 g, 2.66 mmol, 1.00 equiv.) was dissolved in THF (27 mL, 0.10 M), cooled to 0 °C under an atmosphere of nitrogen, and the flask was wrapped with aluminum foil in order to exclude light. Next, NBS (497 mg, 2.79 mmol, 1.05 equiv.) was weighed out in a foil-covered flask and dissolved in THF (11 mL, 0.24 M wrt the silyl enol ether) under an atmosphere of nitrogen. This solution was added to the silyl enol ether at 0 °C via syringe rapidly. The resulting mixture was stirred at 0 °C for 30 minutes, upon which time the reaction was quenched with sat. $NaHCO_3$ (25 mL), and extracted three times with $Et_2O$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude material was purified via flash chromatography on silica gel (9:1 hexanes:EtOAc) affording **2.9** (1.15 g, 86%) as a slightly yellow liquid that was homogeneous by both NMR and TLC. Yield for the two steps: 65%. $R_f$ = 0.48 (6:1 hexanes:EtOAc); $[\alpha]_D$ = –41 (*c* 1.35, $CHCl_3$); IR (neat) 3277, 2953, 2894, 1739, 1575, 1451, 1382, 1276, 1249, 1005, 836, 742, 696; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.37 (ddd, *J* = 10.3, 4.1, 2.5 Hz, 2H), 7.34 – 7.28 (m, 3H), 6.94 (dd, *J* = 7.2, 2.2 Hz, 1H), 5.16 (s, 2H), 4.71 (dd, *J* = 30.0, 7.3 Hz, 2H), 4.42 (dd, *J* = 42.6, 15.0 Hz, 2H), 3.83 – 3.65 (m, 1H), 3.65 – 3.49 (m, 2H), 1.85 (s, 3H), 0.97 – 0.79 (m, 2H), 0.01 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 199.96, 160.97, 144.81, 136.41, 129.69, 128.44, 127.78, 126.78, 119.09, 112.48, 109.86, 90.12, 89.63, 84.07, 77.67, 70.51, 65.93, 34.38,

22.02, 17.93, -1.47; **HRMS**: Exact mass calcd for $C_{25}H_{31}BrO_4Si$ [$(M+H^+)$]: 503.1248; found: 503.1241 (ESI).




***(R)*-tert-butyl 4-(3-methoxy-3-oxoprop-1-yn-1-yl)-2,2-dimethyloxazolidine-3-carboxyl-ate (2.19).** A solution of Garner's aldehyde **2.18** (35.0 g, 0.153 mmol, 1.00 equiv.) in methanol (200 mL, 0.62 M) was treated with the Bestmann-Ohira reagent[83,109] (35.2 g, 0.183 mol, 1.20 equiv.) and cooled to 0 °C. $K_2CO_3$ (40.0 g, 0.289 mol, 1.89 equiv.) was then added in a single portion. The resulting bright yellow suspension was stirred for 14 h, while warming to 23 °C (the cooling bath was allowed to expire). The reaction mixture was diluted with hexanes and treated with sat. aq. $NH_4Cl$ and extracted three times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was combined with the crude from a different batch, which started with 14.7 g (0.0641 mol) of the intermediate alkyne; total material: 49.7 g (0.217 mol). The combined residue was purified by distillation (300 mTorr, 63 °C) to give

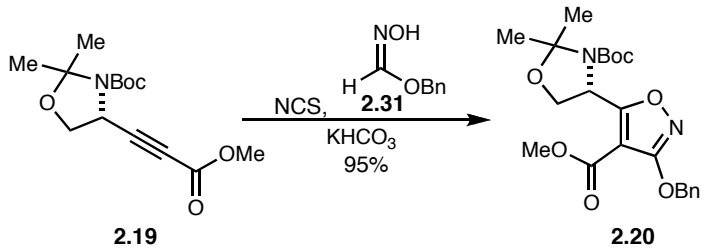
[109] Pietruszka, J.; Witt, A. *Synthesis,* **2006**, 4266-4268.

42.5 g (87%) of the intermediate terminal alkyne. The physical data for this compound were in agreement with data reported in the literature.[110]

A solution of intermediate alkyne (7.10 g, 31.5 mmol, 1.00 equiv.), co-evaporated one time with benzene, in THF (210 mL, 0.15 M) at –78 °C under an atmosphere of argon, was treated with *n*-BuLi (11.0 mL of a 2.92 M solution in hexane, 1.02 equiv.) dropwise over 5 minutes while maintaining the internal temperature < –70 °C. The resulting yellow solution was stirred for 30 minutes, upon which time Mander's reagent[82] (2.55 mL, 32.1 mmol, 1.02 equiv.) was added dropwise over 5 minutes while maintaining the internal temperature at less than –70 °C. The resulting orange solution was stirred at –78 °C for 45 minutes, upon which time the reaction was quenched via the addition of 100 mL of $H_2O$. The reaction was allowed to warm to room temperature with the assistance of a water bath and the resulting clear and slightly brown mixture was extracted three times with hexanes. The combined organic extracts were washed with brine, dried with $Na_2SO_4$, and concentrated *in vacuo*. The residue was purified via flash chromatography on silica gel (4:1 hexanes:$Et_2O$) affording **2.19** (6.27 g, 70%) as a slightly yellow liquid. Yield for the two steps: 61%. This compound was characterized as a ca. 2:3 mixture of boc rotomers. $\boldsymbol{R_f}$ = 0.49 (4:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –129 (*c* 0.60, $CHCl_3$); **IR** (neat) 2982, 2936, 2241, 1706, 1436, 1376, 1260, 1170, 1102, 1054, 901, 845; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 4.71 (s, 0.4H), 4.59 (s, 0.6H), 4.05 (d, *J* = 3.1 Hz, 2H), 3.75 (s, 3H), 1.61 (s, 3H), 1.47 (s, 12H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 153.62, 150.99, 94.79,

[110] Meffre, P.; Gauzy, L.; Branquet, E.; Durand, P. *Tetrahedron,* **1996**, *34*, 11215-11238.

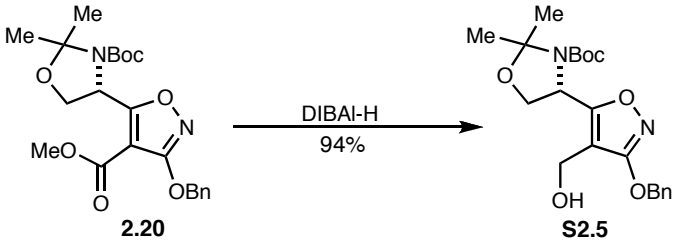
94.27, 85.99, 81.23, 80.91, 73.72, 67.70, 52.67, 48.30, 28.29, 26.88, 25.74, 24.97, 24.23; **HRMS**: Exact mass calcd for $C_{14}H_{21}NO_5$ [(M+$Na^+$)]: 306.1312; found: 306.1322 (ESI).




**2.19** **2.20**

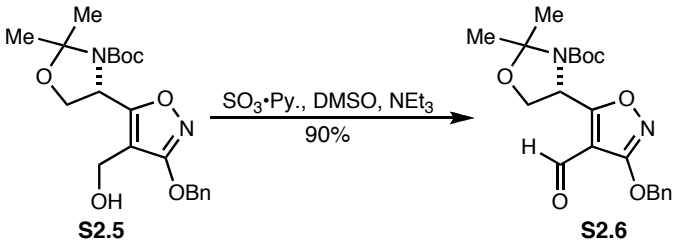
***(S)*-methyl 3-(benzyloxy)-5-(3-(*tert*-butoxycarbonyl)-2,2-dimethyloxazolidin-4-yl) isoxazole-4-carboxylate (2.20).** To a solution of **2.19** (6.15 g, 21.7 mmol, 1.00 equiv.) in EtOAc (110 mL, 0.2 M) at room temperature exposed to air, **2.31** (1.64 g, 10.9 mmol, 0.50 equiv.) was added, followed by the addition of $KHCO_3$ (10.86 g, 109 mmol, 5.00 equiv.) and NCS (1.45 g, 10.9 mmol, 0.50 equiv.). The flask was fitted with a reflux condenser, and the suspension was heated to 48 °C under an atmosphere of nitrogen for 12 h. The reaction was treated with an additional 0.50 equiv. of both **2.31** and NCS every 12 h for a total 5 additions or 2.50 equiv. of each (requiring 60 h of heating at 48 °C). The resulting cloudy and slightly yellow mixture was passed through celite, and the resulting pad of celite was washed with EtOAc. After concentration of the solution *in vacuo*, the resulting solid was purified via flash chromatography on silica gel (12:1 hexanes:EtOAc → 9:1 hexanes:EtOAc) affording **2.20** (8.95 g, 95%) as a white solid that was approximately 95% pure as determined by NMR. $\boldsymbol{R_f}$ = 0.41 (4:1 hexanes:EtOAc, stain: $KMnO_4$). This compound was characterized as a ca. 2:3 mixture of boc rotomers. $\boldsymbol{[\alpha]_D}$ = –37 (*c* 1.65, $CHCl_3$); **IR** (neat) 2979, 1736, 1708, 1618, 1511, 1456, 1377, 1367, 1310, 1263,

1169, 1096, 1070; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.46 (t, *J* = 7.8 Hz, 2H), 7.40 – 7.28 (m, 3H), 5.62 (dd, *J* = 6.6, 1.9 Hz, 0.4H), 5.53 (dd, *J* = 6.8, 2.8 Hz, 0.6H), 5.36 (s, 1H), 5.32 (s, 1H), 4.30 (dd, *J* = 9.4, 6.8 Hz, 1H), 3.97 (dd, *J* = 9.4, 2.6 Hz, 1H), 3.83 (s, 1.8H), 3.80 (s, 1.2H), 1.75 (s, 1.8H), 1.72 (s, 1.2H), 1.59 (s, 1.8H), 1.56 (s, 1.2H), 1.48 (s, 3.7H), 1.26 (s, 5.3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.18, 177.93, 168.85, 168.60, 161.33, 151.75, 150.83, 135.46, 135.36, 128.43, 128.29, 128.22, 127.77, 127.73, 99.94, 99.89, 95.14, 94.57, 81.10, 80.43, 71.73, 71.65, 67.70, 67.57, 55.40, 54.77, 51.85, 51.77, 28.25, 27.97, 25.92, 24.86, 24.64, 23.90; **HRMS**: Exact mass calcd for $C_{22}H_{28}N_2O_7$ [(M+H$^+$)]: 433.1969; found: 433.1975 (ESI).




***(S)-tert*-butyl 4-(3-(benzyloxy)-4-(hydroxymethyl)isoxazol-5-yl)-2,2-dimethyloxazol -idine-3-carboxylate (S2.5).** To a solution of **2.20** (17.6 g, 40.8 mmol, 1.00 equiv.) in toluene (200 mL, 0.2 M) at –78 °C under an atmosphere of argon, DIBAl-H (86.2 mL of a freshly prepared solution from neat DIBAl-H, 1.5 M, 2.50 equiv.) at –78 °C was added against the side of the flask over 15 minutes via cannula. The resulting slightly yellow solution was stirred at –78 °C for 30 minutes, upon which time methanol (41 mL) at –78 °C was added along the side of the flask over 15 minutes (caution, foaming observed upon addition of initial drops of methanol). The resulting cloudy solution was stirred for 15

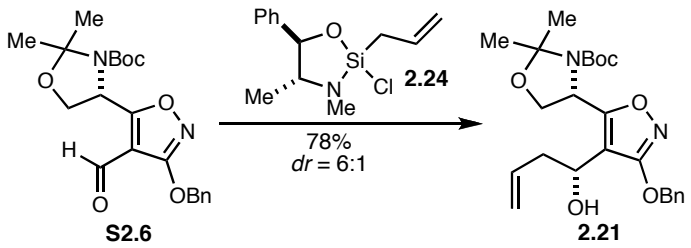
minutes at –78 °C, upon which time it was poured into an Erlenmeyer flask containing 1 *N* HCl (500 mL) at 0 °C. The resulting cloudy mixture was stirred for 15 minutes, upon which time it was extracted four times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (3:1 hexanes:EtOAc → 2.5:1 hexanes:EtOAc) affording **S2.5** (15.5 g, 94%) as a clear liquid. This compound was characterized as a ca. 2:3 mixture of boc rotomers. $\boldsymbol{R_f}$ = 0.17 (3:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –28 (*c* 0.80, $CHCl_3$); **IR** (neat) 3450, 2979, 2881, 1702, 1672, 1513, 1455, 1394, 1367, 1285, 1249, 1169, 1098, 1060, 847; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.40 – 7.31 (m, 3H), 5.33 – 5.25 (m, 2H), 5.19 (d, *J* = 4.5 Hz, 1H), 4.52 (d, *J* = 4.4 Hz, 0.4H), 4.50 (d, *J* = 4.4 Hz, 0.6H), 4.40 (dd, *J* = 13.2, 8.7 Hz, 1H), 4.30 – 4.14 (m, 2H), 3.98 (d, *J* = 3.4 Hz, 1H), 1.65 (s, 2.7H), 1.56 (s, 3.3H), 1.45 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 169.71, 166.60, 152.38, 135.73, 128.48, 128.37, 128.20, 108.43, 94.68, 81.91, 71.47, 65.76, 52.12, 52.00, 28.31, 26.22, 24.81; **HRMS**: Exact mass calcd for $C_{21}H_{28}N_2O_6$ [$(M+H^+)$]: 405.2020; found: 405.2025 (ESI).



**S2.5** **S2.6**

***(S)-tert*-butyl 4-(3-(benzyloxy)-4-formylisoxazol-5-yl)-2,2-dimethyloxazolidine-3-carboxylate (S2.6).** To a solution of **S2.5** (5.50 g, 13.6 mmol, 1.00 equiv.) in $CH_2Cl_2$ (45

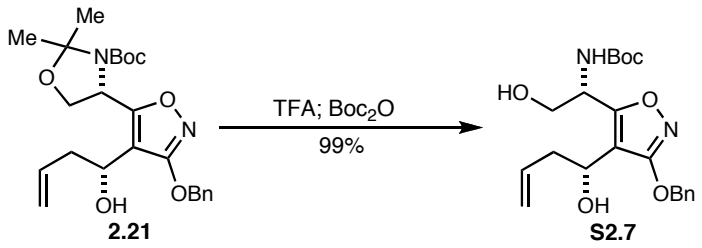
mL, 0.3 M) at 0 °C under an atmosphere of nitrogen, DMSO (8 mL, 1.7 M) was added followed by triethylamine (7.58 mL, 54.4 mmol, 4.00 equiv.). To a second flask, DMSO (20 mL, 2 M wrt $SO_3$•pyr.) was added, followed by $SO_3$•pyr. (6.50 g, 40.8 mmol, 3 equiv.). This mixture was stirred for 5 minutes upon which time most solid had dissolved. Next, the $SO_3$•pyr. solution was added to the solution containing **S2.5** over 5 minutes via syringe. The resulting clear and slightly brown mixture was stirred for 30 minutes at 0 °C, upon which time the reaction was poured directly onto a silica gel column and purified via flash chromatography (6:1 hexanes:EtOAc) affording **S2.6** (4.91 g, 90%) as a clear liquid. This compound was characterized as a ca. 1:1 mixture of boc rotomers. $\boldsymbol{R_f}$ = 0.67 (2:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –55 (*c* 1.3, $CHCl_3$); **IR** (neat) 2978, 2881, 1695, 1604, 1509, 1455, 1366, 1295, 1263, 1168, 1097, 1056, 965, 909; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 9.80 (d, *J* = 1.8 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.44 – 7.35 (m, 3H), 5.56 – 5.49 (m, 0.5H), 5.46 (dd, *J* = 6.7, 2.4 Hz, 0.5H), 5.36 (d, *J* = 20.6 Hz, 2H), 4.33 (dd, *J* = 9.4, 6.8 Hz, 1H), 4.01 – 3.90 (m, 1H), 1.75 (s, 1.6H), 1.71 (s, 1.4H), 1.59 (s, 1.6H), 1.56 (s, 1.4H), 1.49 (s, 4H), 1.28 (s, 5H**). $^{13}$C NMR** (126 MHz, $CDCl_3$) δ 183.34, 183.20, 178.00, 177.56, 169.67, 169.55, 151.81, 150.83, 134.92, 134.83, 128.88, 128.83, 128.68, 128.49, 107.42, 107.22, 95.37, 94.77, 81.34, 80.72, 72.36, 72.29, 67.46, 67.34, 55.28, 54.88, 28.31, 28.09, 26.03, 25.01, 24.67, 23.84; **HRMS**: Exact mass calcd for $C_{21}H_{26}N_2O_6$ [$(M+H^+)$]: 403.1864; found: 403.1868 (ESI).




***(S)-tert*-butyl 4-(3-(benzyloxy)-4-((*R*)-1-hydroxybut-3-en-1-yl)isoxazol-5-yl)-2,2-dimethyloxazolidine-3-carboxylate (2.21).** To a solution of **S2.6** (12.3 g, 30.6 mmol, 1.00 equiv.) in toluene (150 mL, 0.2 M) at –10 °C under an atmosphere of nitrogen, **2.24**[111] (16.4 g, 61.2 mmol, 2.00 equiv.) in toluene (50 mL, 0.6 M wrt **S2.6**) at room temperature was added rapidly via syringe. The reaction was stirred at –10 °C for 84 h, upon which time the reaction was treated with EtOAc (100 mL) and 1 *N* HCl (100 mL) at –10 °C. The reaction was immediately warmed to room temperature and stirred for 20 minutes upon which time the resulting mixture was extracted three times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (4:1 hexanes:EtOAc) to yield **2.21** as a 6:1 mixture of diastereomers (10.58 g, 78%). The mixture of diastereomers was further purified via MPLC (6:1 hexanes:EtOAc → 3:1 hexanes:EtOAc) affording **2.21** (8.57 g, 63%) as a colorless liquid. $\boldsymbol{R_f}$ = 0.54 (3:1 hexanes:EtOAc**);** $\boldsymbol{[\alpha]_D}$ = –30 (*c* 0.80, $CHCl_3$); **IR** (neat) 3425, 2928, 2877, 1688, 1511, 1463, 1388, 1366, 1281, 1252, 1169, 1096, 1067, 915, 847; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.8, 1.0 Hz, 2H), 7.41 – 7.31 (m, 3H), 5.82 (ddd, *J* = 24.2, 10.1, 7.1 Hz, 1H), 5.36 – 5.25 (m, 2H), 5.22 (dd, J =

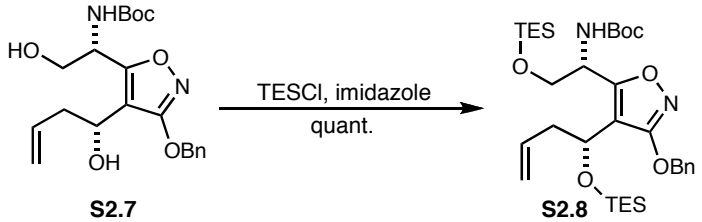
[111] Kinnaird, J. W. A; Ng, P. Y.; Kubota, K.; Wang, X.; Leighton, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 7920-7921.

6.5, 2.4 Hz, 1H), 5.18 – 5.00 (m, 2H), 4.73 (dd, *J* = 12.2, 6.6 Hz, 1H), 4.31 – 4.13 (m, 2H), 2.71 (dd, *J* = 15.2, 6.8 Hz, 2H), 2.51 (s, 1H), 1.65 (s, 3H), 1.55 (s, 3H), 1.45 (s, 7.2H), 1.31 (s, 1.8H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 169.36, 166.22, 152.30, 135.88, 134.77, 128.48, 128.25, 127.90, 117.49, 110.21, 94.64, 81.75, 71.48, 65.93, 64.56, 51.87, 38.86, 28.30, 26.22, 24.87; **HRMS** Exact mass calcd for $C_{24}H_{32}N_2O_6$ [(M+$Na^+$)]: 467.2153; found: 467.2173 (ESI).




***tert*-butyl ((*S*)-1-(3-(benzyloxy)-4-((*R*)-1-hydroxybut-3-en-1-yl)isoxazol-5-yl)-2-hydroxyethyl) carbamate (S2.7).** To a solution of **2.21** (7.80 g, 17.5 mmol, 1.00 equiv.) in methanol (58 mL, 0.3 M) at 0 °C exposed to air, TFA (117 mL, 0.15 M) was added via syringe over 3 minutes. The reaction was stirred at 0 °C for 30 minutes, upon which time the cooling bath was removed and the reaction was allowed to stir for 1.5 h. The reaction was directly concentrated *in vacuo*. The resulting residue was dissolved in dioxane (90 mL, 0.2M) and the solution was cooled to 0 °C while exposed to air. Next, sat. $NaHCO_3$ (170 mL, 0.1 M) was added portion-wise over 3 minutes (caution, gas evolution). The resulting cloudy white solution was stirred vigorously for 1 hour, upon which time $Boc_2O$ (7.64 g, 35 mmol, 2.00 equiv.) was added in a single portion. The reaction was stirred at 0 °C for 2 more h, upon which time the reaction was diluted with $H_2O$ (200 mL) and ex-

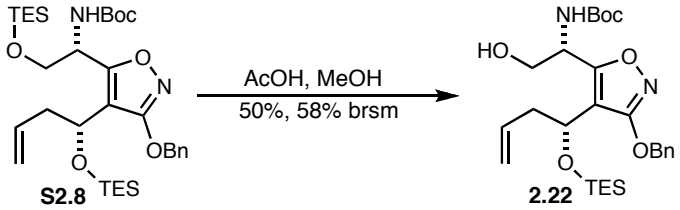
tracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The resulting residue was purified via flash chromatography on silica gel (2:1 hexanes:EtOAc → 1:1 hexanes:EtOAc) affording **S2.7** (7.03 g, 99%) as a colorless liquid. $R_f$ = 0.54 (1:1 hexanes:EtOAc); $[\alpha]_D$ = –32 (*c* 0.55, $CHCl_3$); IR (neat) 3350, 2978, 2935, 1687, 1642, 1521, 1453, 1367, 1252, 1166, 1048, 997, 915, 860; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 5H), 5.79 (dq, *J* = 10.1, 7.0 Hz, 1H), 5.66 (d, *J* = 8.5 Hz, 1H), 5.27 (s, 2H), 5.17 – 4.99 (m, 2H), 4.74 (dt, *J* = 7.7, 5.6 Hz, 1H), 4.03 – 3.88 (m, 1H), 3.88 – 3.78 (m, 1H), 3.06 (s, 1H), 2.60 (qd, *J* = 14.0, 7.4 Hz, 2H), 1.42 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 169.33, 166.72, 155.72, 135.61, 134.02, 128.53, 128.39, 127.96, 127.92, 118.19, 109.65, 80.79, 71.65, 71.61, 64.44, 63.01, 48.44, 40.25, 28.25; **HRMS**: Exact mass calcd for $C_{21}H_{28}N_2O_6$ [(M+H$^+$)]: 405.2020; found: 405.2021 (ESI).




**S2.7** **S2.8**

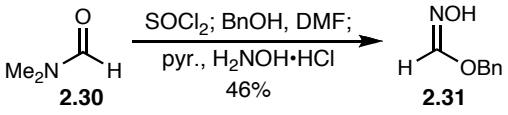
***tert*-butyl ((*S*)-1-(3-(benzyloxy)-4-((*R*)-1-((triethylsilyl)oxy)but-3-en-1-yl)isoxazol-5-yl)-2-((triethylsilyl)oxy)ethyl)carbamate (S2.8).** To a solution of **S2.7** (4.29 g, 10.6 mmol, 1.00 equiv.) in DMF at room temperature under an atmosphere of nitrogen, imidazole (3.61 g, 53.0 mmol, 5.00 equiv.) was added, followed by TESCl (7.10 mL, 42.4 mmol, 4.00 equiv.) over 3 minutes. The resulting clear solution was stirred at room temperature for 12 h, upon which time it was cooled to 0 °C and quenched sequentially with

$H_2O$ (5 mL), sat. $NaHCO_3$ (10 mL), and another portion of $H_2O$ (20 mL) over 5 minutes. The resulting solution was extracted three times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified via flash chromatography on silica gel (9:1 hexanes:EtOAc) affording **S2.8** (6.70 g, quant.) as a colorless liquid. $R_f$ = 0.70 (5:1 hexanes:EtOAc); $[\alpha]_D$ = –6.4 (*c* 0.50, $CHCl_3$); **IR** (neat) 2956, 2912, 2877, 1719, 1509, 1458, 1366, 1241, 1170, 1112, 1005; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 – 7.40 (m, 2H), 7.40 – 7.30 (m, 3H), 5.70 (ddt, *J* = 17.3, 10.2, 7.2 Hz, 1H), 5.50 (d, *J* = 8.9 Hz, 1H), 5.28 (s, 2H), 5.13 – 5.04 (m, 1H), 5.00 (m, 2H), 4.66 (t, *J* = 6.9 Hz, 1H), 3.84 (qd, *J* = 9.9, 5.6 Hz, 2H), 2.56 (ddd, *J* = 31.5, 13.4, 6.7 Hz, 2H), 1.44 (s, 9H), 1.00 – 0.82 (m, 18H), 0.64 – 0.46 (m, 12H). **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 169.32, 167.01, 154.79, 136.09, 134.10, 128.40, 128.15, 127.83, 117.66, 109.21, 79.62, 71.23, 64.83, 64.03, 49.41, 42.78, 28.30, 6.78, 6.69, 6.59, 6.40, 4.57, 4.22; **HRMS**: Exact mass calcd for $C_{33}H_{56}N_2O_6Si_2$ [$(M+H^+)$]: 633.3750; found: 633.3734 (ESI).



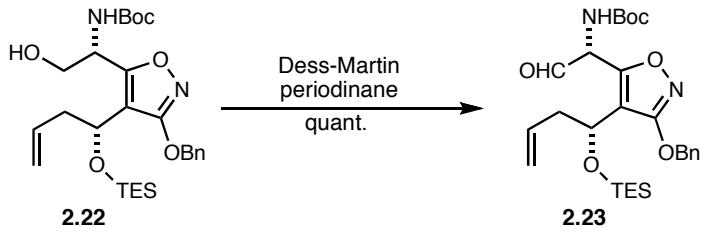

***tert*-butyl ((*S*)-1-(3-(benzyloxy)-4-((*R*)-1-((triethylsilyl)oxy)but-3-en-1-yl)isoxazol-5-yl)-2-hydroxyethyl)carbamate (2.22).** To a solution of **S2.8** (9.50 g, 15.0 mmol, 1.00 equiv.) in methanol (75 mL, 0.2 M) exposed to air at 0 °C, AcOH (0.86 mL, 15.0 mmol, 1.00 equiv.) was added dropwise. The resulting slightly turbid solution was stirred for 2 h at 0 °C, upon which time the cooling bath was removed and the reaction was allowed to

stir for 24 h. The reaction was quenched with sat. $NaHCO_3$ (20 mL) and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (9:1 hexanes:EtOAc → 3:1 hexanes:EtOAc → 2:3 hexanes:EtOAc), affording **2.22** (3.86 g, 50%) as a colorless liquid, diol **S2.7** (1.63 g, 27%), and starting material **S2.8** (1.32 g, 14%). $\boldsymbol{R_f}$ = 0.24 (3:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –8.7 (*c* 1.0, $CHCl_3$); **IR** (neat) 3413, 3334, 2956, 2877, 1712, 1642, 1511, 1461, 1367, 1247, 1169, 1080, 1004; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 5H), 5.79 – 5.59 (m, 2H), 5.27 (s, 2H), 5.18 (dd, *J* = 13.7, 5.6 Hz, 1H), 5.07 – 4.93 (m, 2H), 4.68 (t, *J* = 6.8 Hz, 1H), 3.93 – 3.76 (m, 2H), 2.55 (dd, *J* = 14.4, 7.5 Hz, 3H), 1.45 (s, 9H), 0.89 (t, *J* = 8.0 Hz, 9H), 0.58 (q, *J* = 7.9 Hz, 6H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 169.25, 166.61, 155.53, 135.79, 133.46, 128.49, 128.36, 127.98, 118.16, 109.60, 80.22, 71.52, 65.04, 64.67, 50.01, 42.75, 28.28, 6.66, 4.53; **HRMS**: Exact mass calcd for $C_{27}H_{42}N_2O_6Si$ [$(M+Na^+)$]: 541.2704; found: 541.2705 (ESI).




**benzyl *N*-hydroxyformimidate (2.31).** To DMF (135 mL, 1.75 mol, 1.00 equiv.) at room temperature in a 5 L 3-necked flask equipped with a stirbar, positive nitrogen flow, and an outlet to two consecutive KOH solutions (for $SO_2$ trapping), $SOCl_2$ (127 mL, 1.75 mol, 1.00 equiv.) was added over 15 minutes via syringe. The internal temperature of the solution rose to 35 °C during this addition. Next, the reaction was heated to 40 °C for 2.5

h upon which time the flask was placed under reduced pressure (50 torr) for 3 h (while heated to 40 °C). The resulting slightly yellow mixture was allowed to cool to room temperature and the reaction was stirred for 14 additional h (under reduced pressure) during which time the mixture solidified. The reaction was returned to atmospheric pressure with nitrogen, and the stirbar was replaced with a mechanical stirrer. To the reaction, DMF (1.87 L, 0.938 M) was added rapidly using a funnel, and the reaction was cooled to –40 °C while stirring vigorously. Next, BnOH (181 mL, 1.75 mol, 1.00 equiv.) was added via syringe over 10 minutes while maintaining the internal temperature < –34 °C. During this addition, the suspension became nearly clear and free of particulates. After 5 minutes, hydroxylamine hydrochloride (122 g, 1.75 mol, 1.00 equiv.) was added in a single portion. To the resulting suspension, pyridine (311 mL, 3.85 mol, 2.20 equiv.) was added via funnel (open to air) over 30 seconds. Note: rapid addition of pyridine is critical since prolonged addition dramatically increases the amount of benzyl chloride byproduct formed. The reaction, now with an internal temperature of –34 °C, was warmed quickly to 0 °C with an ice/water bath and stirred for 30 minutes. The reaction was quenched with the addition of 1.5 L of sat. $NaHCO_3$ solution (caution, gas evolution), followed by solid $NaHCO_3$ until solid crashed out of solution and rose to the top of the mixture. The resulting mixture was extracted three times with EtOAc. The combined organic extracts were then dried with $Na_2SO_4$ and concentrated *in vacuo*. The resulting solid was suspended in dichloromethane at 0 °C, and filtered with a fine frit. The solid was then repeatedly washed with cooled dichloromethane until a white solid remained. This procedure yielded **2.31** (121 g, 46%) as a white powder after removal of trace solvent *in vacuo*. The physical data of **2.31** were in agreement with data reported in the literature.[84]




**2.22** **2.23**

***tert*-butyl ((*R*)-1-(3-(benzyloxy)-4-((*R*)-1-((triethylsilyl)oxy)but-3-en-1-yl)isoxazol-5-yl)-2-oxoethyl) carbamate (2.23).** To a solution of **2.22** (1.06 g, 2.05 mmol, 1.00 equiv.) in wet $CH_2Cl_2$ (21 mL, 0.1 M) at room temperature exposed to air, DMP[112] (1.30 g, 3.08 mmol, 1.50 equiv.) was added in a single portion. The reaction was stirred for 35 minutes upon which time the cloudy mixture was poured into an Erlenmeyer flask containing pH 7 phosphate buffer (0.1 M buffer, 100 mL) and $Na_2S_2O_3$ (2.00 g). The reaction flask was washed three times with 10 mL portions of hexanes and this was poured into the vigorously stirring mixture in the Erlenmeyer flask. After 20 minutes of vigorous mixing, the reaction was extracted 3 times with hexanes. The resulting organic extracts were washed 2 times with pH 7 phosphate buffer, and the aqueous (only from second washing with pH 7 buffer) washings were back extracted once with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* to yield a **2.23** (1.06 g, quant.) as a colorless liquid that was used without purification. Note: during concentration, the rotory evaporation bath was kept at 29 °C. This compound was subjected immediately to the fragment coupling reaction (immediately beneath this entry).

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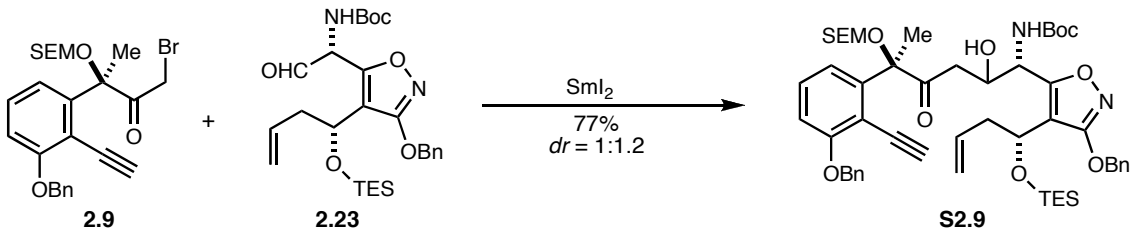
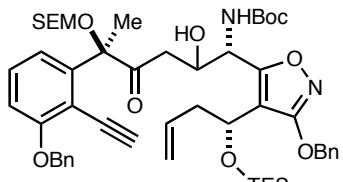
[112] Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155-4156.

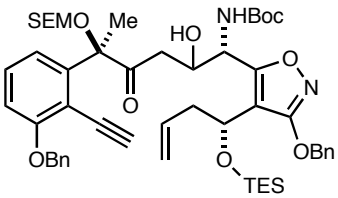



***tert*-butyl ((1*S*,5*R*)-5-(3-(benzyloxy)-2-ethynylphenyl)-1-(3-(benzyloxy)-4-((*R*)-1-((tri-ethylsilyl)oxy) but-3-en-1-yl)isoxazol-5-yl)-2-hydroxy-4-oxo-5-((2-(trimethyl-silyl)eth-oxy)methoxy)hexyl)carbamate (S2.9).** A solution of **2.9** (1.03 g, 2.05 mmol, 1.00 equiv.) and **2.23** (1.06 g, 2.05 mmol, 1.00 equiv.) in THF (41 mL, 0.05 M) at –78 °C under an atmosphere of nitrogen was added to a solution of $SmI_2$ (102 mL of a 0.1 M solution in THF, 5.00 equiv.) at –78 °C via cannula directly into the solution over 10 minutes. The resulting dark blue solution was stirred at –78 °C for 30 minutes, upon which time air was bubbled through a glass pipet directly into the solution at –78 °C for 10 minutes until the blue color disappeared and a yellow color persisted. A solution of sat. $NaHCO_3$ (100 mL) also containing $Na_2S_2O_3$ (10 g) was added and the reaction was allowed to warm to room temperature while stirring vigorously. The mixture was then extracted three times with $Et_2O$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (8:1 hexanes:EtOAc → 6:1 hexanes:EtOAc → 4:1 hexanes:EtOAc) affording **S2.9** (1.48 g of a 1:1.2 mixture of diastereomers, 77%) as a colorless foam. The diastereomers could be separated via MPLC (5:1 hexanes:EtOAc).




**S2.9a** diastereomer #1 (higher Rf)

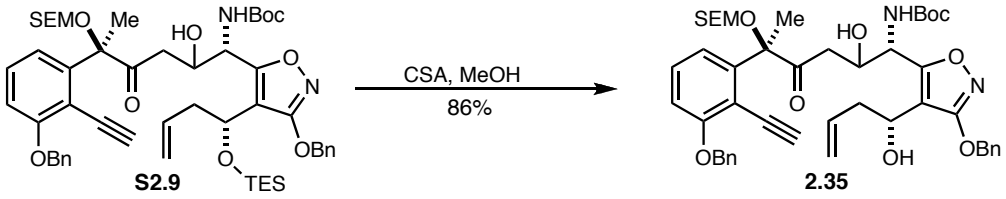
$R_f$ = 0.50 (3:1 hexanes:EtOAc); $[\alpha]_D$ = –34 (*c* 1.3, $CHCl_3$); **IR** (neat) 3436, 3300, 2954, 2877, 1715, 1642, 1575, 1510, 1453, 1367, 1274, 1249, 1168, 1082, 1008, 836, 742; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 2H), 7.43 (d, *J* = 7.0 Hz, 2H), 7.37 (td, *J* = 7.3, 1.4 Hz, 4H), 7.35 – 7.28 (m, 3H), 7.24 (s, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 5.72 (dt, *J* = 17.0, 7.1 Hz, 1H), 5.61 (d, *J* = 9.3 Hz, 1H), 5.28 (s, 2H), 5.14 (s, 2H), 4.99 (m, 3H), 4.84 – 4.60 (m, 3H), 4.39 (s, 1H), 3.70 (td, *J* = 10.1, 6.4 Hz, 1H), 3.60 (dt, *J* = 16.3, 8.1 Hz, 1H), 3.51 (s, 1H), 3.25 (s, 1H), 3.04 (d, *J* = 18.0 Hz, 1H), 2.92 (dd, *J* = 18.3, 9.3 Hz, 1H), 2.69 – 2.41 (m, 2H), 1.79 (s, 3H), 1.41 (s, 9H), 0.89 (t, *J* = 7.9 Hz, 11H), 0.58 (q, *J* = 7.9 Hz, 6H), 0.02 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 209.67, 169.42, 166.19, 160.98, 154.71, 144.92, 136.57, 135.99, 134.14, 129.48, 128.43, 128.37, 128.13, 127.78, 127.72, 126.78, 119.45, 117.61, 112.33, 110.30, 110.05, 90.13, 89.57, 84.72, 79.83, 78.15, 71.21, 70.48, 69.45, 65.75, 64.99, 51.39, 42.60, 41.72, 28.21, 21.79, 17.88, 6.66, 4.46, -1.44; **HRMS**: Exact mass calcd for $C_{52}H_{72}N_2O_{10}Si_2$ [(M+$Na^+$)]: 963.4618; found: 963.4615 (ESI).




**S2.9b** diastereomer #2 (lower Rf)

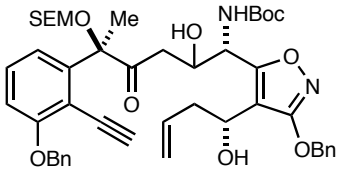
$R_f$ = 0.44 (3:1 hexanes:EtOAc); $[\alpha]_D$ = –27 (*c* 0.45, $CHCl_3$); **IR** (neat) 3413, 3294, 1953, 2868, 1716, 1510, 1452, 1367, 1275, 1250, 1169, 1082, 1011, 836, 742, 696; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.40 (m, 3H), 7.40 – 7.28 (m, 7H), 6.92 (dd, *J* = 6.2, 3.2 Hz, 1H), 5.69 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.51 (d, *J* = 9.5 Hz, 1H), 5.27 (d, *J* = 4.8 Hz, 2H), 5.14 (s, 2H), 5.09 – 4.89 (m,

3H), 4.78 – 4.60 (m, 3H), 4.52 (dd, *J* = 8.2, 3.7 Hz, 1H), 3.75 – 3.66 (m, 1H), 3.59 (dt, *J* = 16.4, 8.2 Hz, 1H), 3.46 (s, 1H), 3.16 (d, *J* = 2.7 Hz, 1H), 2.97 – 2.78 (m, 2H), 2.55 (ddd, *J* = 20.2, 13.6, 6.7 Hz, 2H), 1.77 (s, 3H), 1.40 (s, 9H), 0.87 (t, *J* = 7.9 Hz, 11H), 0.68 – 0.50 (m, 6H), 0.01 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 208.51, 169.55, 166.74, 160.99, 155.23, 145.06, 136.63, 135.98, 134.05, 133.44, 129.55, 128.45, 128.40, 128.18, 127.96, 127.83, 127.75, 126.83, 119.39, 118.16, 117.85, 112.23, 110.05, 109.24, 90.13, 89.36, 84.54, 79.83, 77.90, 71.50, 71.27, 70.48, 69.00, 65.80, 64.70, 51.46, 42.73, 42.46, 41.53, 28.27, 28.23, 21.44, 17.92, 6.72, 6.65, 4.52, -1.42; **HRMS**: Exact mass calcd for $C_{52}H_{72}N_2O_{10}Si_2$ [(M+$Na^+$)]: 963.4618; found: 963.4617 (ESI).



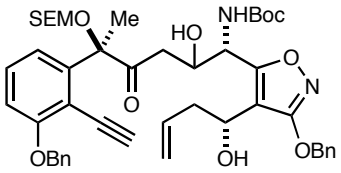

***tert*-butyl ((1S,5R)-5-(3-(benzyloxy)-2-ethynylphenyl)-1-(3-(benzyloxy)-4-((R)-1-hydroxybut-3-en-1-yl)isoxazol-5-yl)-2-hydroxy-4-oxo-5-((2-(trimethylsilyl)ethoxy)-methoxy)hexyl)carbamate (2.35).** To a solution of **S2.9** (903 mg, 0.959 mmol, 1.00 equiv., as a ca. 1:1 mixture of diastereomers) in methanol (9.6 mL, 0.1 M) at 0 °C under an atmosphere of nitrogen, a solution of CSA (22 mg, 0.095 mmol, 0.10 equiv.) dissolved in $CH_2Cl_2$ (2.0 mL, 0.48 M wrt **S2.9**) was added dropwise via syringe over 15 seconds. The resulting solution was stirred for 15 minutes at 0 °C, upon which time the reaction was quenched with sat. $NaHCO_3$ (10 mL), warmed to room temperature, and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and

concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (3:1 hexanes:EtOAc) affording **2.35** (685 mg, 86%) as a colorless foam. The diastereomers could separated at this point via MPLC (3:1 hexanes:EtOAc).



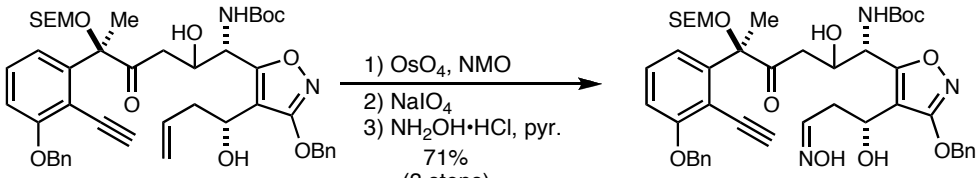

**2.35a** diastereomer #1
(higher Rf)

$R_f$ = 0.33 (2:1 hexanes:EtOAc); $[\alpha]_D$ = –56 (*c* 1.2, $CHCl_3$); **IR** (neat) 3403, 3297, 2952, 2888, 1715, 1509, 1452, 1368, 1274, 1250, 1166, 1026, 918, 835, 742, 696; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.0 Hz, 2H), 7.43 – 7.27 (m, 9H), 7.24 (d, *J* = 8.2 Hz, 1H), 6.93 (d, *J* = 8.3 Hz, 1H), 5.86 – 5.69 (m, 2H), 5.27 (s, 2H), 5.14 (s, 2H), 5.10 – 5.01 (m, 2H), 5.01 – 4.92 (m, 1H), 4.71 (t, *J* = 7.3 Hz, 2H), 4.64 (d, *J* = 7.3 Hz, 1H), 4.39 (s, 1H), 3.90 (d, *J* = 5.6 Hz, 1H), 3.68 (ddd, *J* = 16.0, 9.6, 5.1 Hz, 2H), 3.61 – 3.51 (m, 1H), 3.48 (s, 1H), 2.99 (d, *J* = 18.4 Hz, 1H), 2.83 (dd, *J* = 18.5, 9.3 Hz, 1H), 2.70 – 2.46 (m, 2H), 1.77 (s, 3H), 1.40 (s, 9H), 0.93 – 0.78 (m, 2H), 0.01 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 209.98, 169.26, 165.77, 161.08, 155.10, 144.72, 136.52, 135.77, 134.27, 129.64, 128.51, 128.49, 128.32, 127.88, 127.81, 126.84, 119.42, 117.81, 112.45, 110.83, 110.14, 90.13, 89.57, 84.65, 80.42, 78.19, 71.52, 70.56, 69.24, 65.90, 64.50, 51.13, 41.60, 40.08, 28.25, 21.70, 17.95, -1.42; **HRMS**: Exact mass calcd for $C_{46}H_{58}N_2O_{10}Si$ [$(M+H^+)$]: 827.3934; found: 827.3936 (ESI).




**2.35b** diastereomer #2
(lower Rf)

$R_f$ = 0.29 (2:1 hexanes:EtOAc); $[\alpha]_D$ = –56 (*c* 0.4, $CHCl_3$); **IR** (neat) 3413, 3288, 2952, 1714, 1691, 1510, 1451, 1368, 1274, 1250, 1166, 1020, 836, 742, 696; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.50 – 7.26 (m, 12H), 6.97 – 6.90 (m, 1H), 5.78 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1H), 5.65 (d, *J* = 7.8 Hz, 1H), 5.28 (s, 2H), 5.15 (s, 2H), 5.11 – 4.98 (m, 2H), 4.95 (s, 1H), 4.70 (ddd, *J* = 28.3, 12.4, 6.6 Hz, 3H), 4.54 (s, 1H), 3.90 (d, *J* = 4.8 Hz, 1H), 3.70 (td, *J* = 9.9, 7.0 Hz, 1H), 3.63 – 3.53 (m, 1H), 3.51 (s, 1H), 3.07 (dd, *J* = 18.5, 2.5 Hz, 1H), 2.79 (dd, *J* = 18.6, 9.0 Hz, 1H), 2.74 – 2.48 (m, 2H), 1.75 (s, 3H), 1.38 (s, 9H), 0.92 – 0.77 (m, 2H), 0.01 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 209.69, 169.42, 166.72, 161.05, 155.68, 145.00, 136.54, 135.77, 134.29, 129.63, 128.52, 128.50, 128.32, 127.89, 127.82, 126.87, 119.33, 117.88, 112.34, 110.04, 109.92, 90.09, 89.52, 84.44, 80.53, 78.00, 71.58, 70.53, 67.93, 65.91, 64.44, 50.77, 41.07, 39.58, 28.26, 21.57, 17.91, -1.42; **HRMS**: Exact mass calcd for $C_{46}H_{58}N_2O_{10}Si$ [$(M+H^+)$]: 827.3934; found: 827.3929 (ESI).




**2.35a**
diastereomer #1
(higher Rf)

**2.36a**
diastereomer #1

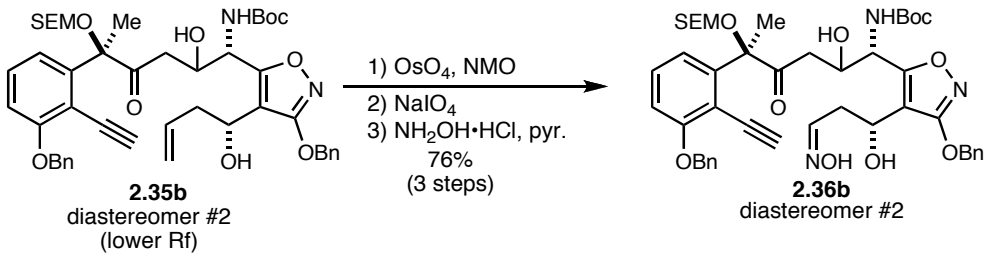
***tert*-butyl ((1S,5R)-5-(3-(benzyloxy)-2-ethynylphenyl)-1-(3-(benzyloxy)-4-((R)-1-hydroxy-3-(hydroxyimino)propyl)isoxazol-5-yl)-2-hydroxy-4-oxo-5-((2-(trimethyl-silyl) ethoxy)methoxy)hexyl)carbamate (2.36a).** To a solution of **2.35a** (350 mg, 0.423

mmol, 1.00 equiv.) in 1:1:1 acetone:pH 7 phosphate buffer:THF (5.7 mL total, 0.056 M) at room temperature exposed to air, NMO (74 mg, 0.635 mmol, 1.50 equiv.) was added, followed by $OsO_4$ (265 μL of a 2.5 wt% solution in *t*-BuOH, 0.05 equiv.). Upon addition of $OsO_4$ the reaction turned from turbid to clear and yellow. The reaction was stirred for 2.5 h at room temperature, upon which time it was cooled to 0 °C and a sat. $NaHCO_3$ solution (10 mL) containing 100 mg $NaHSO_3$ was added. The reaction quickly turned brown after this addition. The cooling bath was removed, and the reaction was stirred for 5 minutes. The resulting mixture was diluted with $H_2O$ (10 mL) and extracted four times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* to afford a brown foam. $\boldsymbol{R_f}$ = 0.17 (1:1 hexanes:EtOAc).

The brown foam was immediately dissolved in a 3:1 mixture of THF:pH 7 phosphate buffer (8.5 mL total, 0.05 M) at room temperature exposed to air, and $NaIO_4$ (271 mg, 1.27 mmol, 3.00 equiv.) was added in a single portion. The reaction became cloudy upon this addition. After stirring for 1 hour at room temperature, the reaction was diluted with $H_2O$ (10 mL), and extracted one time with $CH_2Cl_2$. To the remaining aqueous layer, brine was added (20 mL) and it was extracted three more times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* to afford a brown foam. $\boldsymbol{R_f}$ = 0.58 (1:1 hexanes:EtOAc).

The brown foam was dissolved in absolute ethanol (8.5 mL, 0.05 M) at room temperature exposed to air, and pyridine (423 μL, 1.0 M wrt **2.35a**) was added, followed by hydroxylamine hydrochloride (88 mg, 1.27 mmol, 3.00 equiv.). The resulting solution was stirred for 1.75 h, upon which time the reaction was cooled to 0 °C and sat. $NH_4Cl$

(10 mL) was added. The reaction was then diluted with $H_2O$ (10 mL), and extracted three times with $Et_2O$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (1:1 hexanes:EtOAc) affording **2.36a** (255 mg, 71%) as a white foam and a ca. 1:1 mixture of *E* and *Z* oxime isomers. $\boldsymbol{R_f}$ = 0.50 (1:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –42 (*c* 1.5, $CHCl_3$); IR (neat) 3372, 3294, 2953, 2883, 1713, 1694, 1512, 1453, 1368, 1274, 1250, 1164, 1026, 836, 744, 696; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.28 (m, 10.5H), 7.25 – 7.19 (m, 2H), 6.93 (d, *J* = 8.3 Hz, 1H), 6.91 – 6.84 (m, 0.5H), 6.02 (d, *J* = 8.8 Hz, 0.5H), 5.75 (d, *J* = 8.4 Hz, 0.5H), 5.27 (s, 2H), 5.14 (s, 2H), 4.96 (ddd, *J* = 22.3, 14.4, 6.0 Hz, 2H), 4.82 – 4.58 (m, 3H), 4.42 (s, 1H), 4.30 (d, *J* = 6.4 Hz, 0.5H), 4.02 (d, *J* = 4.8 Hz, 0.5H), 3.76 – 3.61 (m, 2H), 3.55 (dt, *J* = 15.0, 4.7 Hz, 2H), 3.11 – 2.62 (m, 4H), 1.77 (d, *J* = 5.8 Hz, 3H), 1.40 (d, *J* = 5.4 Hz, 9H), 0.86 (ddd, *J* = 9.8, 6.7, 3.1 Hz, 2H), 0.08 – -0.08 (m, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 209.89, 169.15, 166.16, 165.86, 161.09, 155.29, 149.14, 148.64, 144.67, 136.52, 135.66, 135.61, 129.64, 128.54, 128.52, 128.49, 128.37, 128.35, 127.96, 127.91, 127.81, 126.84, 119.43, 112.53, 110.57, 110.19, 90.12, 89.79, 89.74, 84.85, 84.62, 80.66, 78.18, 71.68, 70.56, 69.13, 65.94, 62.32, 51.29, 51.11, 41.78, 41.63, 35.02, 31.60, 28.25, 21.75, 21.62, 17.92, -1.43; **HRMS**: Exact mass calcd for $C_{45}H_{57}N_3O_{11}Si$ [$(M+H^+)$]: 844.3835; found: 844.3822 (ESI).




**2.35b**
diastereomer #2
(lower Rf)

**2.36b**
diastereomer #2

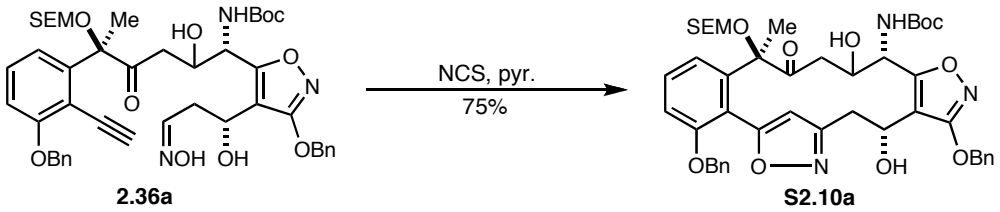
***tert*-butyl ((1S,5R)-5-(3-(benzyloxy)-2-ethynylphenyl)-1-(3-(benzyloxy)-4-((R)-1-hydroxy-3-(hydroxyimino)propyl)isoxazol-5-yl)-2-hydroxy-4-oxo-5-((2-(trimethyl silyl)ethoxy)methoxy)hexyl)carbamate (2.36b).** To a solution of **2.35b** (285 mg, 0.345 mmol, 1.00 equiv.) in 1:1:1 acetone:pH 7 phosphate buffer:THF (3.5 mL total, 0.1 M) at room temperature exposed to air, NMO (61 mg, 0.518 mmol, 1.50 equiv.) was added, followed by $OsO_4$ (216 μL of a 2.5 wt% solution in *t*-BuOH, 0.05 equiv.). Upon addition of $OsO_4$ the reaction turned from turbid to clear and yellow. The reaction was stirred for 2.5 h at room temperature, upon which time it was cooled to 0 °C and a sat. $NaHCO_3$ solution (10 mL) containing 100 mg $NaHSO_3$ was added. The reaction quickly turned brown after this addition. The cooling bath was removed, and the reaction was stirred for 5 minutes. The resulting mixture was diluted with $H_2O$ (10 mL) and extracted four times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* to afford a brown foam. $\boldsymbol{R_f}$ = 0.12 (1:1 hexanes:EtOAc).

The brown foam was immediately dissolved in a 3:1 mixture of THF:pH 7 phosphate buffer (6.9 mL total, 0.05 M) at room temperature exposed to air, and $NaIO_4$ (221 mg, 1.04 mmol, 3.00 equiv.) was added in a single portion. The reaction soon became cloudy after this addition. After stirring for 1 hour at room temperature, the reaction was diluted with $H_2O$ (10 mL), and extracted one time with $CH_2Cl_2$. To the remaining aqueous layer, brine was added (20 mL) and it was extracted three more times with $CH_2Cl_2$.

The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* affording a brown foam. $\boldsymbol{R_f}$ = 0.51 (1:1 hexanes:EtOAc).

The brown foam was dissolved in absolute ethanol (6.9 mL, 0.05 M) at room temperature exposed to air, and pyridine (345 μL, 1.0 M wrt **2.35b**) was added, followed by hydroxylamine hydrochloride (71 mg, 1.04 mmol, 3.00 equiv.). The resulting solution was stirred for 1.75 h, upon which time the reaction was cooled to 0 °C and sat. $NH_4Cl$ (10 mL) was added. The reaction was then diluted with $H_2O$ (10 mL) and extracted three times with $Et_2O$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The resulting residue was purified via flash chromatography on silica gel (1:1 hexanes:EtOAc) affording **2.36b** (221 mg, 76%) as a white foam and a ca. 2:1 mixture of *E* and *Z* oxime isomers. This compound was homogeneous by NMR and TLC, however NMR spectroscopic analysis is complicated due to three rotational isomers in addition to two oxime isomers; only peak shifts and coupling constants ($^1$H NMR) are tabulated. $\boldsymbol{R_f}$ = 0.53 (1:1 hexanes:EtOAc) $[\alpha]_D$ = –49 (*c* 0.40, $CHCl_3$); **IR** (neat) 3370, 3292, 2950, 2894, 1711, 1694, 1575, 1510, 1452, 1368, 1274, 1251, 1164, 1018, 836, 742, 696; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 6.01 (dd, *J* = 35.8, 9.1 Hz), 5.69 (dd, *J* = 25.9, 7.4 Hz), 5.35 – 5.21 (m), 5.14 (d, *J* = 4.1 Hz), 5.05 (s), 4.95 (ddd, *J* = 23.7, 12.7, 5.8 Hz), 4.77 – 4.61 (m), 4.59 (s), 4.53 (s), 4.43 (s), 4.29 (s), 4.14 (s), 3.86 (d, *J* = 34.5 Hz), 3.77 – 3.62 (m), 3.62 – 3.40 (m), 3.12 (dd, *J* = 47.3, 19.0 Hz), 3.02 – 2.88 (m), 2.81 (ddd, *J* = 31.7, 19.1, 9.6 Hz), 2.61 (dd, *J* = 16.3, 5.8 Hz), 1.75 (d, *J* = 6.2 Hz), 1.38 (d, *J* = 9.0 Hz), 0.85 (ddd, *J* = 9.5, 5.2, 1.9 Hz), 0.00 (td, *J* = 3.4, 2.0 Hz**); $^{13}$C NMR** (126 MHz, $CDCl_3$) δ 210.13, 209.44, 169.24, 166.81, 161.00, 160.97, 155.81, 155.26, 148.89, 148.77, 148.49, 148.33, 144.97, 144.77, 136.49, 135.62, 135.57, 129.57, 129.43, 128.48, 128.46, 128.43,

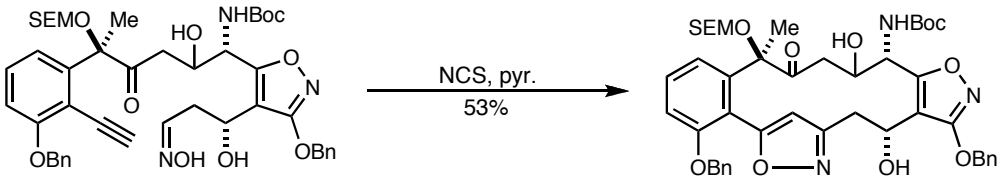
128.34, 128.29, 128.26, 127.99, 127.87, 127.82, 127.76, 126.82, 126.80, 119.46, 119.25, 112.40, 112.30, 110.28, 109.97, 109.58, 109.45, 89.97, 89.67, 89.61, 84.79, 84.53, 84.46, 84.35, 80.68, 80.61, 78.09, 77.96, 71.65, 71.62, 70.46, 69.11, 67.72, 67.52, 65.89, 62.31, 62.07, 50.98, 50.74, 41.58, 41.08, 34.66, 31.86, 31.37, 28.20, 21.58, 21.38, 17.83, 17.80, -1.47, -1.49, -1.68; **HRMS**: Exact mass calcd for $C_{45}H_{57}N_3O_{11}Si$ [$(M+K^+)$]: 882.3394; found: 882.3350 (ESI).




**2.36a** **S2.10a**

**Macrocycle S2.10a.** To a solution of **2.36a** (244 mg, 0.289 mmol, 1.00 equiv.) in $CHCl_3$ (29 mL, 0.01 M) at room temperature under argon, pyridine (70 μL, 0.867 mmol, 3 equiv.) was added via syringe, followed by NCS (41 mg, 0.303 mmol, 1.05 equiv., freshly recrystallized from benzene). The reaction was immediately sealed and heated to 60 °C for 46 h. The resulting slightly yellow solution was concentrated directly *in vacuo*. The residue was purified via flash chromatography on silica gel (2:1 hexanes:EtOAc) affording **S2.10a** (183 mg, 75%) as a white foam. NMR spectroscopic analysis is complicated due to peak broadening from slow rotation of the macrocycle; only peak shifts and coupling constants ($^1$H NMR) will be reported. $\boldsymbol{R_f}$ = 0.81 (1:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –108 (*c* 1.3, $CHCl_3$); **IR** (neat) 3400, 2952, 1712, 1640, 1608, 1512, 1452, 1368, 1273, 1249, 1165, 1060, 1017, 860, 837; **$^1$H NMR** (500 MHz, Acetone) δ 7.60 (bs), 7.49 (t, *J* = 8.2 Hz), 7.41 (t, *J* = 7.3 Hz), 7.37 – 7.22 (m), 7.20 (bs), 6.84 (bs), 6.34 (bs), 6.25 (bs), 5.92

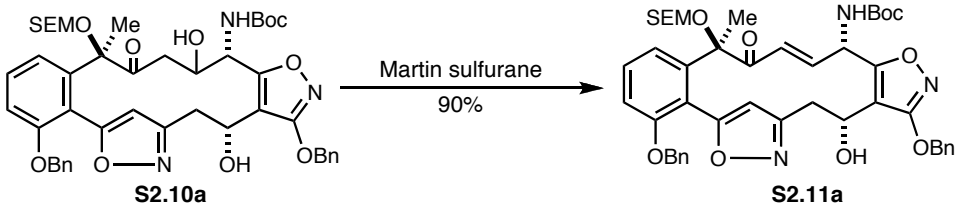
(bs), 5.37 (bs), 5.09 (bs), 4.99 (bs), 4.81 – 4.00 (m), 3.73 (s), 3.42 (s), 3.10 (s), 2.92 – 2.45 (m), 2.07 (s), 1.77 (bs), 1.68 (bs), 1.40 (s), 1.10 – 0.65 (m), 0.03 (s); **$^{13}$C NMR** (126 MHz, Acetone) δ 213.09, 170.85, 169.49, 167.50, 160.92, 159.17, 158.41, 155.90, 155.27, 144.57, 137.76, 137.12, 131.92, 131.55, 129.20, 129.04, 128.60, 128.33, 127.49, 121.80, 119.89, 114.36, 113.36, 110.38, 109.66, 108.77, 91.60, 90.66, 86.12, 85.62, 79.88, 72.34, 72.03, 70.84, 66.14, 64.82, 53.06, 41.10, 32.15, 31.60, 28.37, 26.36, 23.14, 18.53, -1.32; **HRMS**: Exact mass calcd for $C_{45}H_{55}N_3O_{11}Si$ [$(M+H^+)$]: 842.3679; found: 842.3668 (ESI).




**2.36b** **S2.10b**

**Macrocycle S2.10b.** To a solution of **2.36b** (22 mg, 0.263 mmol, 1.00 equiv.) in $CHCl_3$ (26 mL, 0.01 M) at room temperature under argon, pyridine (64 μL, 0.789 mmol, 3 equiv.) was added via syringe, followed by NCS (37 mg, 0.276 mmol, 1.05 equiv., freshly recrystallized from benzene). The reaction was immediately sealed and heated to 60 °C for 72 h. The resulting slightly yellow solution was concentrated directly *in vacuo*. The residue was purified via flash chromatography on silica gel (2:1 hexanes:EtOAc → 1:1 hexanes:EtOAc) affording **S2.10b** (118 mg, 53%) as a white foam. $\boldsymbol{R_f}$ = 0.23 (1:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –59 (*c* 0.55, $CHCl_3$); **IR** (neat) 3380, 2951, 2897, 1712, 1679, 1510, 1453, 1367, 1273, 1246, 1017, 859, 836; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.3 Hz, 2H), 7.46 – 7.33 (m, 5H), 7.31 – 7.21 (m, 3H), 7.16 (d, *J* = 7.9 Hz, 1H), 7.11 (d, *J* =

6.5 Hz, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.16 (bs, 1H), 5.95 (s, 1H), 5.37 (dd, *J* = 30.2, 11.7 Hz, 2H), 5.24 (s, 1H), 5.04 – 4.85 (m, 2H), 4.69 (s, 1H), 4.50 (dd, *J* = 49.2, 7.7 Hz, 2H), 4.10 (s, 1H), 3.69 (dd, *J* = 17.4, 9.2 Hz, 2H), 3.40 (dd, *J* = 17.1, 8.8 Hz, 1H), 3.04 (s, 1H), 2.47 (d, *J* = 8.4 Hz, 1H), 2.24 (s, 1H), 1.70 (s, 3H), 1.35 (s, 9H), 0.93 – 0.69 (m, 2H), 0.03 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 215.13, 169.11, 166.84, 166.56, 159.18, 158.37, 156.93, 142.46, 136.74, 136.19, 131.05, 128.77, 128.61, 128.58, 128.52, 127.86, 126.59, 121.13, 118.08, 113.38, 108.60, 107.14, 90.75, 85.58, 81.20, 72.12, 70.35, 69.52, 65.87, 65.35, 55.06, 40.97, 32.33, 28.44, 23.60, 18.41, -1.16; **HRMS**: Exact mass calcd for $C_{45}H_{55}N_3O_{11}Si$ [$(M+H^+)$]: 842.3679; found: 842.3673 (ESI).

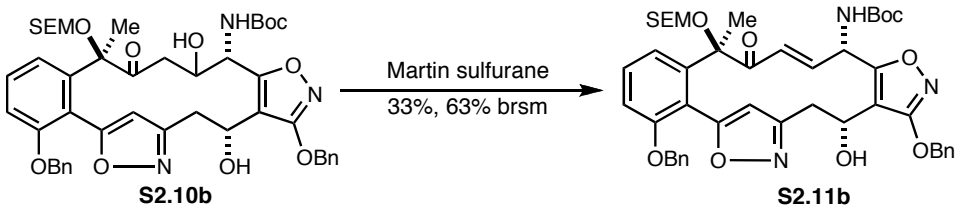



**S2.10a** **S2.11a**

**Macrocyclic-enone S2.11a.** To **S2.10a** (175 mg, 0.208 mmol, 1.00 equiv.) in $CH_2Cl_2$ (6.9 mL, 0.03 M) at –78 °C under an atmosphere of nitrogen, the Martin sulfurane[113] (6.1 mL of a 0.054 M solution in $CH_2Cl_2$, 1.6 equiv.) at room temperature was added along the side of the flask over 1 minute. The resulting pale yellow solution was stirred at –78 °C for 12 minutes, upon which time it was warmed to –55 °C. The reaction was held at this temperature for 45 minutes, during which time the reaction became bright yellow. The

[113] Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5003-5010.

reaction was quenched via the addition of sat. $NaHCO_3$ (10 mL), warmed to room temperature while stirring vigorously, and extracted with three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography (3:1 hexanes:EtOAc) affording **S2.11a** (155 mg, 90%) as a colorless oil. $R_f$ = 0.42 (2:1 hexanes:EtOAc); $[\alpha]_D$ = –97 (*c* 0.80, $CHCl_3$); **IR** (neat) 3360, 2953, 1712, 1511, 1452, 1367, 1272, 1250, 1166, 1016, 744, 695; **$^1$H NMR** (500 MHz, DMSO) δ 7.86 (bs, 1H), 7.76 – 7.65 (m, 2H), 7.62 – 7.43 (m, 5H), 7.43 – 7.32 (m, 2H), 7.32 – 7.12 (m, 4H), 6.87 (bs, 1H), 6.55 (bs, 1H), 6.32 (bs, 1H), 5.61 (bs, 1H), 5.43 (s, 1H), 5.34 (q, *J* = 12.4 Hz, 2H), 5.18 – 4.96 (m, 2H), 4.84 (bs, 1H), 4.73 (bs, 1H), 4.58 (bs, 1H), 3.61 (d, *J* = 5.4 Hz, 1H), 3.46 – 3.30 (m, 2H), 2.98 (bs, 1H), 1.63 (s, 3H), 1.37 (s, 9H), 0.94 – 0.57 (m, 2H), -0.04 (s, 9H); **$^{13}$C NMR** (126 MHz, DMSO) δ 200.43, 166.52, 164.89, 158.26, 157.54, 154.34, 145.88, 142.56, 139.92, 136.73, 136.19, 131.05, 130.68, 129.46, 128.37, 128.28, 128.21, 128.05, 127.55, 126.64, 124.06, 120.45, 117.26, 113.47, 109.61, 106.97, 89.74, 83.67, 78.81, 70.88, 69.32, 64.87, 61.84, 49.21, 31.70, 28.05, 22.36, 17.48, -1.41; **HRMS**: Exact mass calcd for $C_{45}H_{53}N_3O_{10}Si$ [$(M+H^+)$]: 824.3573; found: 824.3582 (ESI).




**S2.10b** **S2.11b**

**Macrocyclic-enone S2.11b.** To **S2.10b** (55 mg, 0.065 mmol, 1.00 equiv.) in $CH_2Cl_2$ (2.2 mL, 0.03 M) at –78 °C under an atmosphere of nitrogen, the Martin sulfurane[114] (2.2 mL of a 0.053 M solution in $CH_2Cl_2$, 1.8 equiv.) at room temperature was added along the side of the flask over 2 minutes during which time the internal temperature was kept less than –68 °C. The resulting pale yellow solution was stirred at –78 °C for 15 minutes, upon which time it was warmed to –55 °C. The reaction was held at this temperature for 30 minutes, during which time the reaction became bright yellow. The reaction was then allowed to warm to –40 °C over 30 additional minutes, and to 0 °C over 1 hour. The reaction was quenched via the addition of sat. $NaHCO_3$ (5 mL), warmed to room temperature while stirring vigorously, and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography (3:1 hexanes:EtOAc) affording **S2.11b** (18 mg, 33%) as a colorless oil in addition to **S2.10b** (26 mg, 47%). The spectroscopic data for **S2.11b** matched the data for the previous dehydration reaction employing **S2.10a** as substrate.

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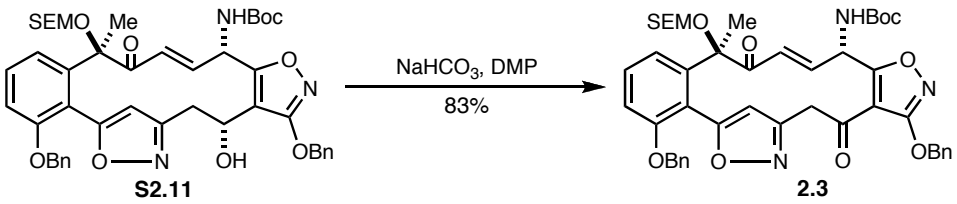
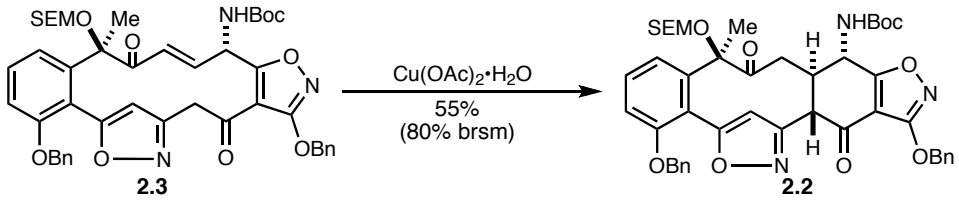
[114] Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 5003-5010.




**Macrocyclic-enone 2.3.** To a solution of **2.3** (155 mg, 0.188 mmol, 1.00 equiv.) in wet $CH_2Cl_2$ (6.3 mL, 0.03 M), $NaHCO_3$ (240 mg, 2.86 mmol, 15.2 equiv.) was added, followed by DMP (120 mg, 0.282 mmol, 1.50 equiv.) in a single portion. The reaction was stirred for 35 minutes, upon which time more DMP (25 mg, 0.0589 mmol, 0.313 equiv.) was added. The reaction was stirred for 25 additional minutes, upon which time the reaction was poured into an Erlenmeyer flask containing sat. $NaHCO_3$ (20 mL) and $Na_2S_2O_3$ (190 mg). The original reaction flask was washed liberally with hexanes and these washings were poured into the vigorously mixing solution. After 10 minutes, the mixture was poured into a sep. funnel, the organic layer was removed, and the remaining aqueous layer was extracted two times more with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (4:1 hexanes:EtOAc) affording **2.3** (129 mg, 83%) as a colorless oil. $R_f$ = 0.73 (2:1 hexanes:EtOAc); $[\alpha]_D$ = –93 (*c* 0.40, $CHCl_3$); **IR** (neat) 1393, 2956, 1717, 1596, 1504, 1453, 1368, 1272, 1164, 1013, 837, 744, 696; **$^1$H NMR** (500 MHz, DMSO) δ 7.91 (d, *J* = 6.4 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.50 (t, *J* = 8.2 Hz, 2H), 7.42 (m, 2H), 7.35 – 7.28 (m, 3H), 7.28 – 7.21 (m, 4H), 6.65 (d, *J* = 15.5 Hz, 1H), 6.41 – 6.29 (m, 1H), 6.27 (s, 1H), 5.74 (t, *J* = 8.5 Hz, 1H), 5.43 (q, *J* = 11.9 Hz, 2H), 5.10 (dd, *J* = 29.8, 12.7 Hz, 2H), 4.57 (dd, *J* = 34.4, 6.5 Hz, 2H), 4.32 (d, *J* = 11.3 Hz, 1H), 3.83 (d, *J* = 11.5 Hz, 1H), 3.60 (td, *J* = 10.1, 6.3 Hz, 1H), 3.40 (dt, *J* = 16.0, 8.0 Hz, 1H), 1.60 (s, 3H), 1.39 (s, 9H), 0.88 – 0.65 (m, 2H), -0.03 (s, 9H); **$^{13}$C NMR** (126 MHz, DMSO) δ 199.46, 189.30,

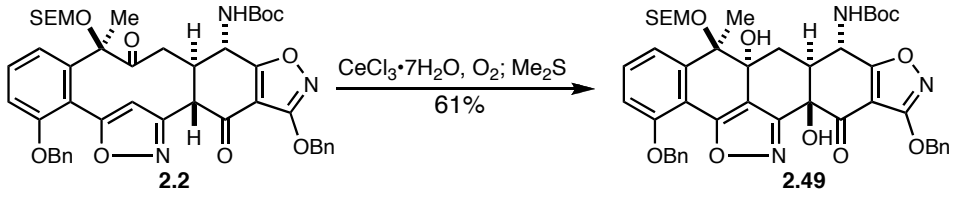
175.36, 168.00, 166.41, 157.51, 155.49, 154.59, 151.37, 142.48, 137.95, 136.65, 135.32, 131.02, 128.51, 128.29, 128.03, 127.62, 126.78, 123.79, 120.86, 116.34, 113.57, 107.93, 107.78, 89.60, 83.85, 79.21, 72.15, 69.49, 65.01, 50.37, 38.65, 28.00, 22.10, 17.53, -1.46; **HRMS**: Exact mass calcd for $C_{45}H_{51}N_3O_{10}Si$ [$(M+H^+)$]: 822.3417; found: 822.3421 (ESI).




**2.3** **2.2**

**Transannular Michael product 2.2.** To **2.3** (29 mg, 0.035 mmol, 1.0 equiv.) in degassed methanol (3.5 mL, 0.01 M) at room temperature under an atmosphere of argon, $Cu(OAc)_2•H_2O$ (21 mg, 0.105 mmol, 3.00 equiv.) was added in a single portion. The reaction was immediately sealed and placed in a cooling bath at 0 °C for 65 h. The reaction was quenched with sat. $NH_4Cl$ (5 mL), diluted with $H_2O$ (5 mL), and extracted three times with $CH_2Cl_2$. The combined organics were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (3:1 hexanes:EtOAc → 2:1 hexanes:EtOAc) affording **2.2** (16 mg, 55%) as a colorless oil. Additionally, **2.3** (9.0 mg, 31%) was recovered. $\boldsymbol{R_f}$**(28)** = 0.33 (2:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –152 (*c* 0.50, $CHCl_3$); **IR** (neat) 3335, 2954, 2893, 2470, 2361, 1705, 1619, 1514, 1482, 1454, 1409, 1369, 1250, 1166, 1052, 1015, 860, 835; $^1$**H NMR** (500 MHz, Benzene) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 2H), 7.07 – 7.00 (m, 2H), 6.97 (dd, *J* = 15.5, 8.1 Hz, 2H), 6.93 – 6.86 (m, 4H), 6.59 (dd, *J* = 7.4, 1.7 Hz, 1H), 5.28 (dd, *J* = 25.3, 12.1 Hz, 2H), 4.79 (t, *J* = 15 Hz, 1H), 4.72 (d, *J* = 8.4 Hz, 2H), 4.55 (d, *J* = 7.4

Hz, 1H), 4.34 (d, *J* = 7.4 Hz, 1H), 3.96 (d, *J* = 10.4 Hz, 1H), 3.76 – 3.65 (m, 1H), 3.40 – 3.27 (m, 2H), 2.72 (d, *J* = 11.5 Hz, 1H), 2.59 (dd, *J* = 22.3, 11.2 Hz, 1H), 2.23 (d, *J* = 16.6 Hz, 1H), 1.46 (s, 3H), 1.39 (s, 9H), 0.94 – 0.79 (m, 2H), 0.03 (s, 9H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 202.63, 183.06, 179.03, 170.47, 168.24, 159.77, 158.02, 156.14, 144.91, 136.76, 135.87, 130.77, 128.81, 128.70, 128.69, 128.59, 127.47, 127.11, 121.73, 118.45, 113.88, 111.49, 108.38, 90.25, 85.25, 80.19, 72.27, 70.93, 65.84, 54.04, 49.59, 49.13, 35.98, 28.18, 24.21, 18.25, -1.29; **$^{1}$H NMR** (600 MHz, *d*6-acetone) δ 7.57 – 7.53 (m, 2H), 7.51 (t, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.40 – 7.34 (m, 3H), 7.33 – 7.27 (m, 2H), 7.25 (s, 1H), 6.79 (d, *J* = 9.6 Hz, 1H), 5.42 – 5.33 (m, 2H), 5.27 (q, *J* = 12.2 Hz, 2H), 5.20 (t, *J* = 10.4 Hz, 1H), 4.74 (dd, *J* = 23.6, 7.3 Hz, 2H), 4.38 (d, *J* = 11.5 Hz, 1H), 3.85 (dd, *J* = 17.0, 11.0 Hz, 1H), 3.72 (td, *J* = 9.9, 6.3 Hz, 1H), 3.44 (td, *J* = 10.0, 6.3 Hz, 1H), 2.90 (q, *J* = 11.4 Hz, 1H), 2.33 (d, *J* = 16.9 Hz, 1H), 1.64 (s, 3H), 1.46 (s, 9H), 0.96 – 0.69 (m, 2H), -0.01 (s, 9H); **HRMS**: Exact mass calcd for $C_{45}H_{51}N_3O_{10}Si$ [$(M+H^+)$]: 822.3417; found: 822.3402 (ESI).

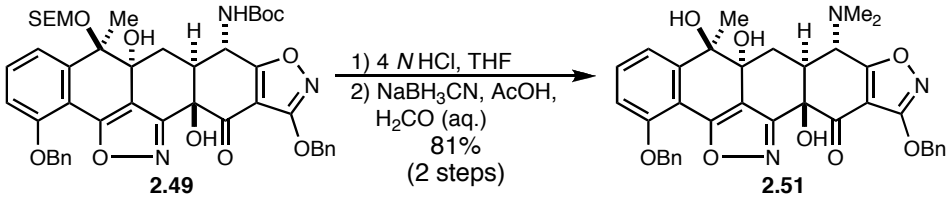



**Linear pentacycle 2.49.** To **2.2** (16 mg, 0.0195 mmol, 1.0 equiv.) at room temperature in isopropanol (1.9 mL, 0.01 M), $O_2$ (from a balloon) was bubbled through the solution for 10 minutes. Next, $CeCl_3$•$7H_2O$ (3.6 mg, 9.8 μmol, 0.50 equiv.) was added to the solution and the reaction was stirred vigorously while $O_2$ was continuously bubbled through the

solution (a 21 gauge needle that was slightly blocked to reduce flow was used as an outlet). The reaction was stirred for 1 hour, during which time the solution became slightly yellow. Next, the reaction was immediately transferred to a silica gel column pre-equilibrated with EtOAc, and the reaction was passed through the column with 25 mL of EtOAc. The resulting solution was concentrated *in vacuo*.

The crude mixture was immediately dissolved in $CH_2Cl_2$ (1.9 mL, 0.01 M) at room temperature under an atmosphere of nitrogen, and dimethyl sulfide (8.0 μL, 0.16 mmol, 8.0 equiv) was added directly into the solution. The resulting clear solution was stirred at room temperature for 15 minutes, upon which time the reaction was concentrated directly *in vacuo*. The crude material was purified via column chromatography on silica gel (2:1 hexanes:EtOAc), and further purified via preparatory HPLC (1.8% *i*-PrOH/hexanes), affording **2.49** (10 mg, 61%) as a white solid. $\boldsymbol{R_f}$ = 0.33 (2:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –38 (*c* 0.34, $CHCl_3$); **IR** (neat) 3481, 3264, 2951, 2893, 1692, 1619, 1514, 1454, 1368, 1275, 1248, 1157, 1018, 836; **$^1$H NMR** (600 MHz, *d*6-acetone) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.54 (d, *J* = 7.7 Hz, 2H), 7.46 – 7.39 (m, 5H), 7.37 (t, *J* = 8.2 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.04 (s, 1H), 5.45 – 5.27 (m, 5H), 4.41 (s, 1H), 4.34 (d, *J* = 7.3 Hz, 1H), 4.27 (d, *J* = 7.3 Hz, 1H), 3.48 – 3.39 (m, 1H), 3.13 (dt, *J* = 15.9, 8.0 Hz, 2H), 2.64 (t, *J* = 12.8 Hz, 1H), 2.17 (dd, *J* = 13.1, 2.0 Hz, 1H), 1.82 (s, 3H), 1.51 (s, 9H), 0.79 – 0.64 (m, 2H), -0.05 (s, 9H); **$^{13}$C NMR** (126 MHz, THF) δ 185.64, 181.84, 169.48, 163.34, 159.49, 156.77, 155.77, 141.88, 138.25, 137.04, 130.72, 129.19, 129.11, 128.91, 128.77, 128.29, 127.54, 122.54, 118.31, 115.95, 114.33, 105.88, 90.59, 81.73, 79.54, 75.32, 72.39, 70.97, 68.95, 67.93,

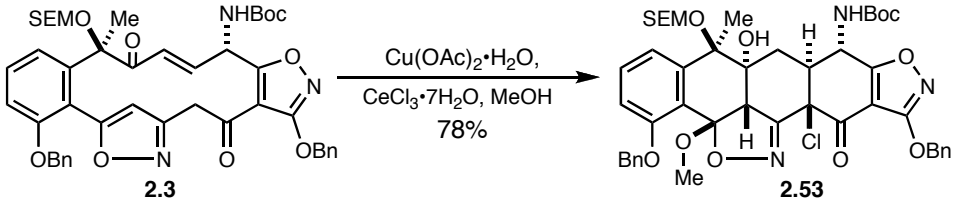
65.43, 48.49, 28.65, 25.81, 18.63, 16.55, -1.19; **HRMS**: Exact mass calcd for $C_{45}H_{51}N_3O_{11}Si$ [$(M+H^+)$]: 838.3366; found: 838.3377 (ESI).




**Tertiary amine 2.51.** To a solution of **2.49** (6.5 mg, 7.8 μmol, 1.0 equiv.) in THF (1.5 mL, 0.0052 M) at room temperature exposed to air, 4 *N* HCl (1.5 mL, 0.0052 M) was added rapidly. The reaction was then sealed and stirred for 20 h at room temperature. The resulting solution was neutralized via the addition of sat. $NaHCO_3$ (10 mL, caution, gas evolution) and extracted three times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*.

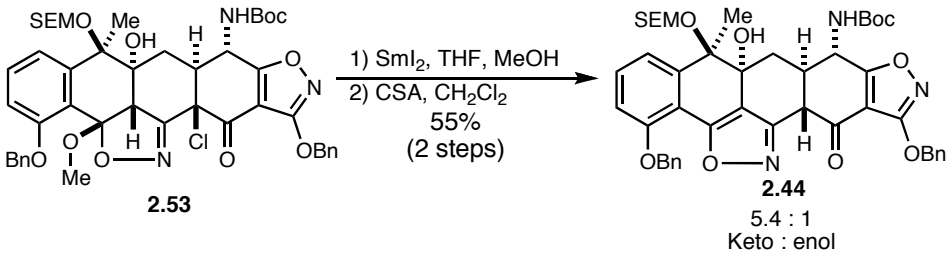
The crude material was immediately dissolved in acetonitrile (1.5 mL, 0.0052 M) at room temperature exposed to air, and $H_2CO$ (0.75 mL of a 37% aq. Solution) was added. Next, acetic acid (2.0 μL, 0.039 mmol, 5.0 equiv.) was added, followed by $NaBH_3CN$ (2.5 mg, 0.039 mmol, 5.0 equiv.), and the reaction was stirred at room temperature for 15 minutes. The reaction was quenched via the addition of sat. $NaHCO_3$ (5 mL) and extracted three times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was first purified via flash chromatography (2:1 EtOAc:hexanes), and further purified via preparatory HPLC (5% *i*-PrOH/hexanes), affording **2.51** (4.0 mg, 81%, 2) as a white solid over two steps. $\boldsymbol{R_f}$ = 0.46

(2:1 EtOAc:hexanes); $[\alpha]_D$ = –41 (*c* 0.31, $CHCl_3$); **IR** (neat) 3379, 2934, 2803, 1712, 1652, 1602, 1574, 1513, 1474, 1454, 1372, 1274, 1026, 987, 911, 859; **$^1$H NMR** (500 MHz, THF) δ 7.63 – 7.57 (m, 2H), 7.53 – 7.47 (m, 2H), 7.40 – 7.33 (m, 3H), 7.33 – 7.22 (m, 4H), 7.10 (dd, *J* = 7.3, 2.0 Hz, 2H), 6.15 (d, *J* = 1.3 Hz, 1H), 5.42 – 5.20 (m, 4H), 4.28 (s, 1H), 4.21 (d, *J* = 10.2 Hz, 1H), 4.17 (s, 1H), 3.00 (td, *J* = 9.3, 5.4 Hz, 1H), 2.57 (s, 6H), 2.44 – 2.38 (m, 2H), 1.69 (s, 3H); **$^{13}$C NMR** (126 MHz, THF) δ 186.19, 184.80, 169.41, 163.29, 159.99, 155.51, 146.82, 138.42, 137.05, 131.25, 129.17, 129.13, 128.93, 128.79, 128.24, 127.56, 120.38, 118.08, 115.43, 113.45, 107.42, 75.95, 75.44, 72.48, 70.90, 69.40, 67.93, 61.17, 44.93, 28.08, 25.81, 20.07; **HRMS**: Exact mass calcd for $C_{36}H_{33}N_3O_8$ [(M+H$^+$)]: 636.2340; found: 636.2336 (ESI).




**C12a-Chloride 2.53.** To a solution of **2.3** (56 mg, 68 μmol, 1.0 equiv.) in degassed methanol (3.4 mL, 0.020 M) at room temperature under an atmosphere of argon, $Cu(OAc)_2•H_2O$ (34 mg, 0.17 mmol, 2.5 equiv.) was added, followed by $CeCl_3•7H_2O$ (127 mg, 0.34 mmol, 5.0 equiv.). Following addition of $CeCl_3•7H_2O$, the color of the reaction changed from blue to slightly yellow. The reaction was stirred under an atmosphere of argon for 22 h during which time the color of the reaction became progressively more green. The reaction was poured into a 125 mL Erlenmeyer flask containing sat. $NaHCO_3$ (20 mL), and the biphasic mixture was stirred vigorously for 5 minutes. The mixture was

then transferred to a separatory funnel and extracted three times with $CH_2Cl_2$. The combined organic extracts were washed one time with brine, dried with $Na_2SO_4$, and concentrated *in vacuo*. The resulting residue was purified via flash chromatography (2:1 hexanes:EtOAc), affording **2.53** (47 mg, 78%) as a colorless oil. $R_f$ = 0.36 (2:1 hexanes:EtOAc); $[\alpha]_D$ = –45 (*c* 0.31, $CHCl_3$); **IR** (neat) 3362, 2953, 1717, 1615, 1580, 1516, 1479, 1455, 1370, 1290, 1250, 1162, 1073, 1022, 861, 836; **$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.43 – 7.28 (m, 7H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.09 (d, *J* = 8.3 Hz, 1H), 5.37 (q, 2H), 5.16 (q, *J* = 11.7 Hz, 2H), 4.93 (d, *J* = 9.9 Hz, 1H), 4.60 – 4.49 (m, 2H), 4.37 (s, 1H), 3.65 (td, *J* = 10.4, 5.7 Hz, 1H), 3.34 (s, 3H), 3.14 (s, 1H), 2.37 (t, *J* = 12.7 Hz, 1H), 2.28 – 2.14 (m, 1H), 1.72 (s, 3H), 1.64 – 1.44 (m, 9H), 0.87 – 0.70 (m, 2H), -0.08 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 178.50, 177.84, 168.89, 159.09, 155.62, 137.06, 136.45, 135.14, 130.98, 128.76, 128.70, 128.67, 121.52, 120.86, 115.17, 105.56, 90.83, 81.59, 78.23, 77.50, 77.45, 77.24, 76.99, 76.78, 76.55, 72.45, 70.86, 67.99, 65.64, 54.99, 51.52, 49.50, 48.45, 29.14, 28.46, 18.26, 17.73, -1.20; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 888.3289; found: 888.3277 (ESI).




**Keto/Enol 2.44.** To a solution of $SmI_2$ (2.1 mL of a 0.10 M solution in THF, 0.21 mmol, 10 equiv.) at –78 °C under an atmosphere of argon, **2.53** (19 mg, 0.0214 mmol, 1.00

equiv.) in a degassed 1:1 mixture of THF and methanol (1.5 mL each, 0.0071 M total) at room temperature was added rapidly via cannula. The resulting blue/green solution was stirred at –78 °C for 40 minutes, upon which time air was blown through the solution until a yellow color persisted. Next, a solution of sat. $Na_2S_2O_3$ (5 mL) was added and the reaction was warmed to room temperature while stirring vigorously. The solution was poured into a separatory funnel, diluted with water (5 mL) and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography (2:1 hexanes:EtOAc), affording des-Cl-**2.53** (12 mg, 78%) as a colorless oil.

To a solution of des-Cl-**2.53** (8.0 mg, 0.0094 mmol, 1.0 equiv.) in $CH_2Cl_2$ (1.8 mL, 0.0050 M) at room temperature exposed to air, CSA (2.2 mg, 0.0094 mmol, 1.0 equiv.) was added in a single portion. The reaction was stirred at room temperature for 1.5 h, upon which time the reaction was quenched via addition of pH 7 phosphate buffer (5 mL), and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography (1:1 hexanes:EtOAc), affording **2.44** (6.4 mg, 83%) as a colorless oil. Yield for the two steps: 55%. $\boldsymbol{R_f}$ = 0.23 (2:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –57 (*c* 0.45, $CHCl_3$); **IR** (neat) 3392, 2952, 1714, 1652, 1614, 1573, 1506, 1480, 1454, 1368, 1247, 1165, 1059, 1016, 836; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.15 (s, 7H), 6.92 (t, *J* = 8.1 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 5.24 (s, 1H), 4.99 – 4.80 (m, 2H), 4.36 (d, *J* = 7.5 Hz, 1H), 4.19 (d, *J* = 7.4 Hz, 1H), 4.06 (d, *J* = 10.1 Hz, 1H), 3.58 – 3.48 (m, 1H), 3.24 – 3.12 (m, 1H), 2.95 (d, *J* = 12.3 Hz, 1H), 2.60 – 2.43 (m, 1H), 2.21 (d, *J* = 3.9 Hz, 1H), 1.75 (s, 3H), 1.44 (s, 9H), 0.81 (ddd, *J* = 10.1, 6.4, 3.3 Hz,

2H), 0.01 (s, 9H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 182.57, 179.54, 168.03, 162.88, 155.71, 155.14, 154.85, 140.25, 136.84, 135.77, 130.18, 128.86, 128.81, 128.74, 128.59, 128.55, 128.51, 128.49, 128.43, 128.41, 128.20, 128.09, 128.00, 127.90, 127.81, 127.71, 127.51, 127.40, 127.24, 126.96, 121.98, 116.96, 115.31, 114.02, 108.13, 90.14, 80.90, 79.93, 72.04, 70.55, 68.75, 65.15, 50.92, 49.31, 42.57, 31.35, 28.32, 28.16, 18.11, 16.27, -1.38, -1.44; **HRMS**: Exact mass calcd for [$(M+Na^+)$]: 844.3236; found: 844.3230 (ESI).

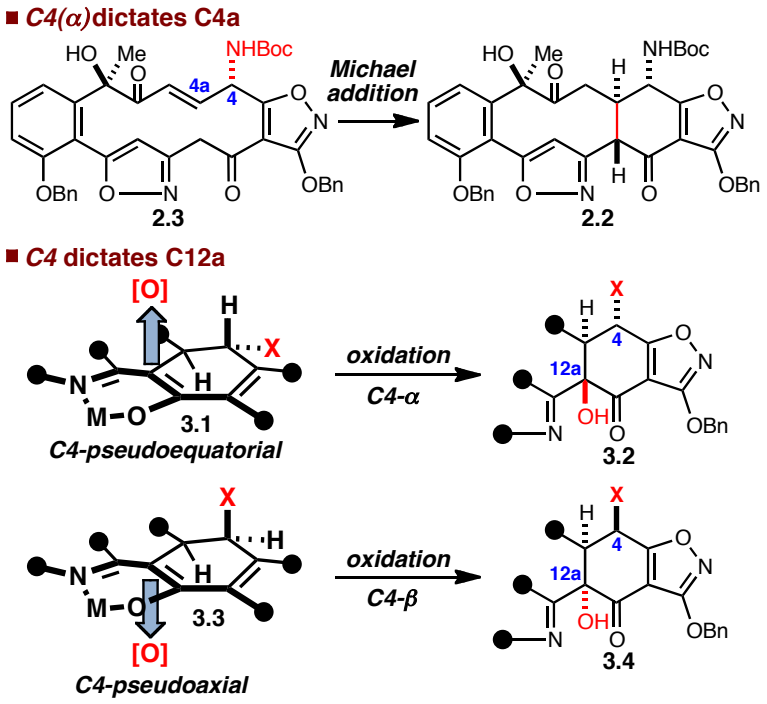
# *Chapter 3*

## Synthesis of the Second Generation Macrocycle

### I. Revision of the Synthesis Plan

The established requirement for the C- and B-rings of the tetracycline core to be intact prior to C12a-hydroxylation forced us to reassess our overall synthesis plan. Of particular importance to any new strategy was the incorporation of our validated Michael reaction while also allowing for flexibility later in the route to tackle hydroxylation. At this point, we knew that the C4-stereocenter was appropriate to facilitate construction of the C4a-stereocenter via a Michael addition (**2.3** to **2.2**, Scheme 3.1). Additionally, we knew that this same C4-stereocenter directs C12a-hydroxylation to the incorrect face, producing an epimeric C12a-tertiary carbinol (**3.1** to **3.2**). Therefore, in order to proceed with the synthesis we needed to identify an appropriate substrate for successful C12a-oxidation, and engineer it into our synthesis plan.

**Scheme 3.1** Stereochemical relationships for the Michael- and C12a-hydroxylation reactions.




Literature reports of both successful and unsuccessful C12a-oxidations, while at times contradictory or ambiguous, generally hinted at the requirement for the C4-substituent to be pseudoaxial, meaning it must be of opposite stereochemistry to that of tetracycline (**3.3** to **3.4**).[42-44,115] This was unfortunate, since selective inversion of an amino-stereocenter is not a trivial task, especially on a highly functionalized substrate.[116] Further, epimerization at C4 following the transannular Michael addition was not an option at this point since the NHBoc group resides in the thermodynamically favored pseudoequatorial position. An additional concern was that not all C12a-oxidations fit the

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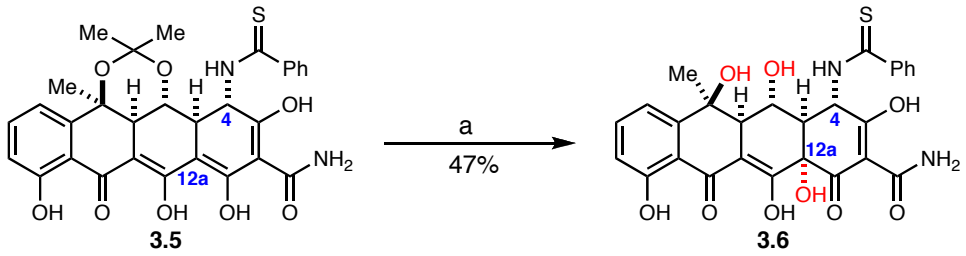
[115] (a) Holmlund, C. E.; Andres, W. W.; Shay, A. J. *J. Am. Chem. Soc.* **1959**, *81*, 4748-4749. (b) Muxfelt, H.; Kreutzer, A. *Naturwissenschafien* **1959**, *46*, 204-205. (c) Muxfeldt, H.; Buhr, G.; Banger, R. *Angew. Chem. Int. Ed.* **1962**, *3*, 157. (d) Gurevich, A. I.; Karapetyan, M. G.; Kolosov, M. N. *Khim. Prirodn. Soedin.* **1966**, *2*, 141-142.

[116] (a) Sørbye, K.; Tautermann, C.; Carlsen, P.; Fiksdahl, A. *Tet. Asymm.* **1998**, *9*, 681-689. (b) Said, S. A.; Fiksdahl, A. *Tet. Asymm.* **2001**, *12*, 1947-1951.

model, since the reaction performed by Muxfeldt and co-workers in the synthesis of (±)-terramycin seems to counter the idea that an axial C4-substituent directs oxidation to the opposite face (Scheme 3.2).

**Scheme 3.2** Oxidation of the C12a-position executed by Muxfeldt and co-workers[44]




Reagents and conditions: (a) $O_2$, NaH, $P(OEt)_3$, THF, DMF, $H_2O$, rt; 0.01 *N* HCl/MeOH; 47%.

## II. The Development of a Predictive Tool

While the general model for C12a-oxidation depicted in Scheme 3.1 stands to chemical intuition, given the Muxfeldt case, we felt that more insight was needed in order to completely justify route revision. Unfortunately transition state calculations were considered unfeasible since the computational study of reactions involving lanthanides is sufficiently complicated,[117] and the mechanism of cerium-catalyzed hydroxylation has not been studied in detail. Thus, we considered a simplified alternative involving the hypothetical chlorination of an enolate at C12a (Figure 3.1).[118] While we were not interested in obtaining a barrier height for this reaction (indeed, this reaction would presumably proceed

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[117] Eisenstein, O.; Maron, L. *J. Organomet. Chem.* **2002**, *647*, 190-197.

[118] $Cl_2$ was chosen as the electrophile since it represents the smallest molecule capable of reacting with an enolate other than $F_2$. Due to the small nature of $Cl_2$, we were hopeful that it would lend greater insight into the reactivity profile of the substrate without any major contribution from the electrophile (this would not be the case with larger electrophiles such as NCS). $F_2$ was not chosen since it was possible that this molecule would give anomalous results due to the exceedingly high electronegativity. Later halogens such as $Br_2$ were not chosen simply to reduce the computational cost associated with this tool.

without barrier), we were interested in obtaining an energy profile as the C12a position changes hybridization from $sp^2$ to $sp^3$. Importantly, since data regarding the selectivity of hydroxylation at C12a is available, the results of this tool could be compared with actual examples therefore establishing whether the output is meaningful. Lastly, this tool is meant to give a binary sense of selectivity, no quantification was considered possible despite the energy values gathered from the computational data.

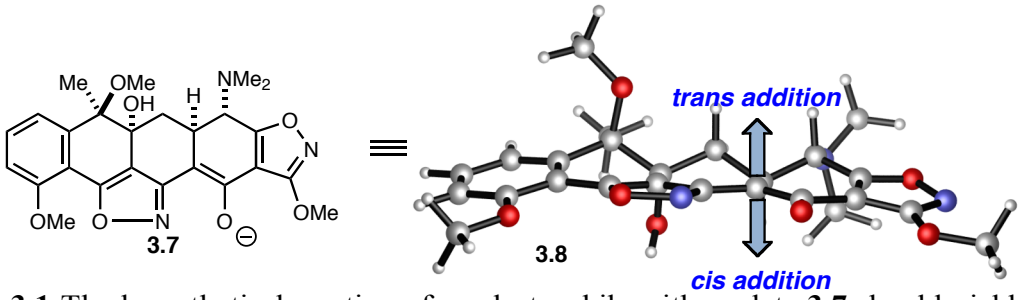



**Figure 3.1** The hypothetical reaction of an electrophile with enolate **3.7** should yield insight into substrate biases.

Enolates **3.7** and **3.12** were initially optimized via DFT in the absence of $Cl_2$ (Figure 3.2). In parallel subsequent computational experiments, $Cl_2$ was forced via distance restriction to approach the enolate to form either a *cis* or *trans* C12a-chloride. The energy profile of each intermediate distance (0.1 Å iterations from a C-Cl bond-length of 3.5 – 2.1 Å) was plotted, and the two approaches to the enolate face were compared.

Initially the C12a-chlorination of both the equatorial and axial dimethylamine enolates were computed as we tried to determine whether the dimethylamine moiety is the major determinant of C12a-hydroxylation diastereoselectivity. As the data in Figure 3.2 reveals, the C4-dimethylamine does control facial selectivity, as evidenced by the fact that the trajectory of $Cl_2$ is lower in energy at all points for the *trans* addition with an equatorial amine, versus the preference for *cis* addition in the presence of an axial amine.

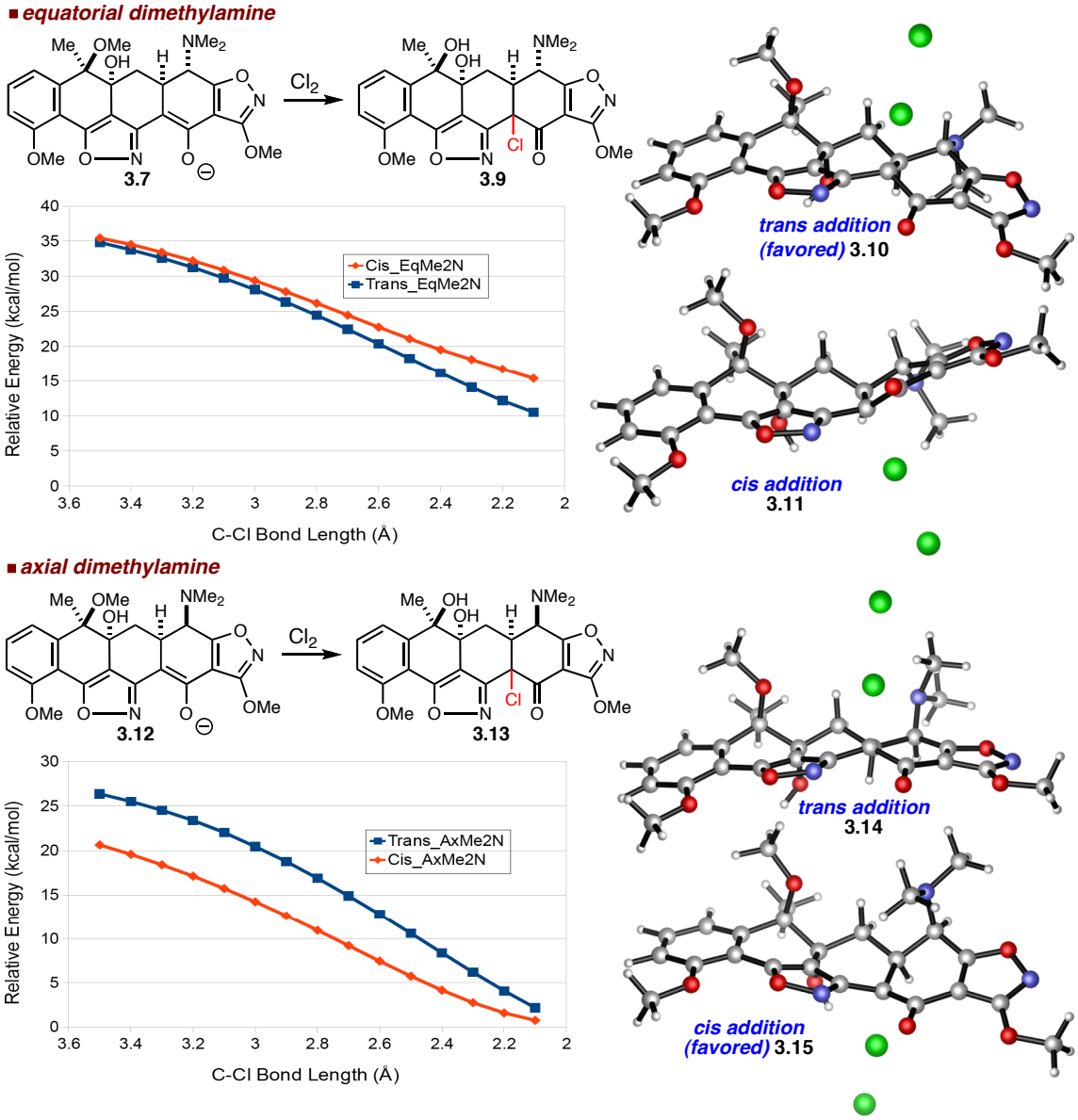



**Figure 3.2** Computational analysis of C12a-chlorination reveals substrate stereochemical biases. Green spheres are chlorine atoms approaching the enolate. Each structure represents enolate chlorination with a C-Cl distance of 2.1 Å.[119] The chloride counterion has been purposefully omitted in the reaction equations to simplify the figure.

[119] The B3LYP hybrid functional with the 6-31G* basis set was used. M. J. Frisch.; *et al.* Gaussian, Inc., Pittsburgh, PA, 2006.

With computational data in support of the model proposed in Scheme 3.1, we next looked at the Muxfeldt example while employing the same enolate chlorination analysis (Figure 3.3). In this case, the data revealed that chlorination to form a *cis* ring fusion was favored, in agreement with the experimental result of enolate hydroxylation. Importantly, energy minimized structures with a C-Cl bond distance of 2.1 Å provide an explanation for the seeming defiance of the model. Due to the acetonide protecting the C5- and C6-hydroxyl functions, the molecule is geared in such a way that oxidation at C12a would proceed with a significant energetic penalty (**3.17**). Alternatively, reaction to form a *cis* ring fusion enables bond formation to occur from the convex face of the structure (**3.18**). With the data from these computational experiments coupled with chemical intuition, we felt confident that the relationship between the C4-substituent and oxidation at C12a was understood. Therefore, attention returned to the incorporation of this information into our larger synthesis plan.[120]

[120] A reasonable criticism is that the computational experiments are quite removed from actual experimental conditions, thus reducing their overall utility. However, at the time we were quite confounded by the C12a-hydroxylation dilemma considering the Muxfeldt case in comparison to the other literature examples. While in retrospect simple molecular modeling may have been sufficient, the results of these com-

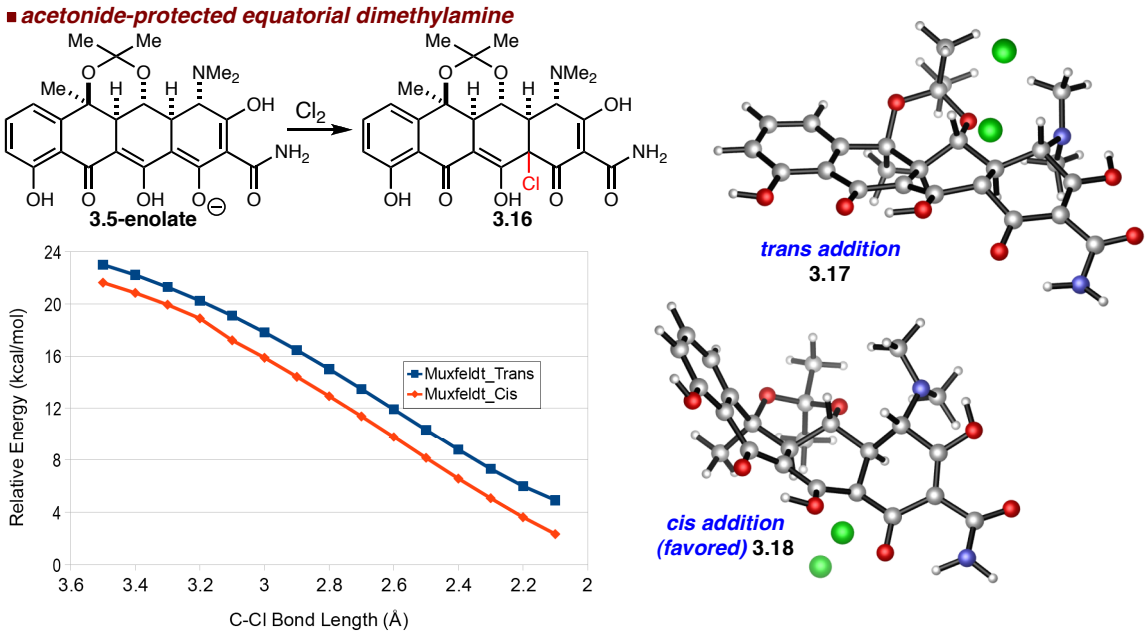



**Figure 3.3** Computational analysis of C12a-chlorination as it applies to the Muxfeldt case.[44] Green spheres are chlorine atoms approaching the enolate. Each structure represents enolate chlorination with a C-Cl distance of 2.1 Å.[121] The chloride counterion has been purposefully omitted in the reaction equations to simplify the figure.

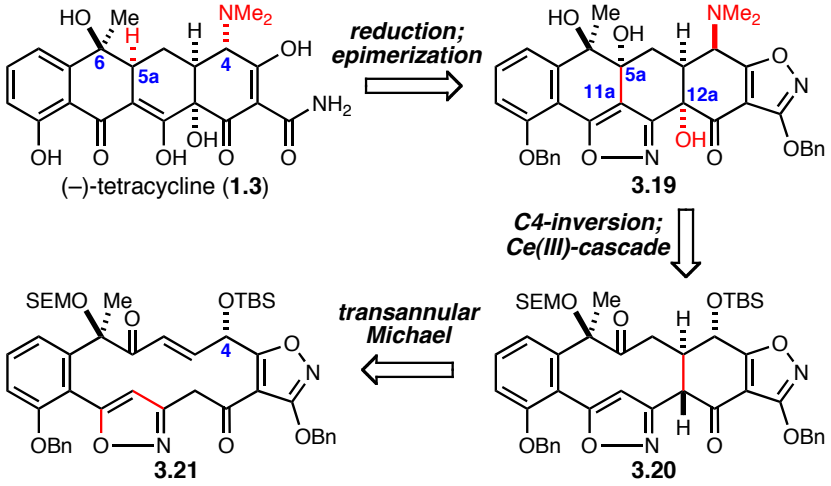
## III. Synthesis Plan

Following our studies of C12a-oxidation, we decided it would be best to introduce a readily modifiable substituent at C4, such that a late-stage stereochemical inversion at this position may be performed (Scheme 3.3). Substitution of the C4-NHBoc group with a silyl-protected alcohol (**3.21**) was therefore proposed since this should maintain the stereochemical relationship between C4 and C4a during the Michael addition, while also providing the flexibility that we would need to intercept a competent substrate for hydroxylation. When activated, the hydroxyl function may be stereospecifically displaced with a

putations assuaged our concerns significantly. Any ability to become more certain about a transformation that requires a significant time commitment to even test was welcomed at this juncture.

nucleophilic nitrogen source, such as dimethylamine or azide, producing the requisite inverted C4 stereocenter. Hydroxylation should then proceed to form **3.19**. Lastly, a late-stage epimerization[42] of the labile C4-stereocenter and hydrogenation should yield tetracycline.

**Scheme 3.3** Revised synthesis plan to tetracycline employing the late-stage installation of a C4-dimethylamine with stereochemical inversion.



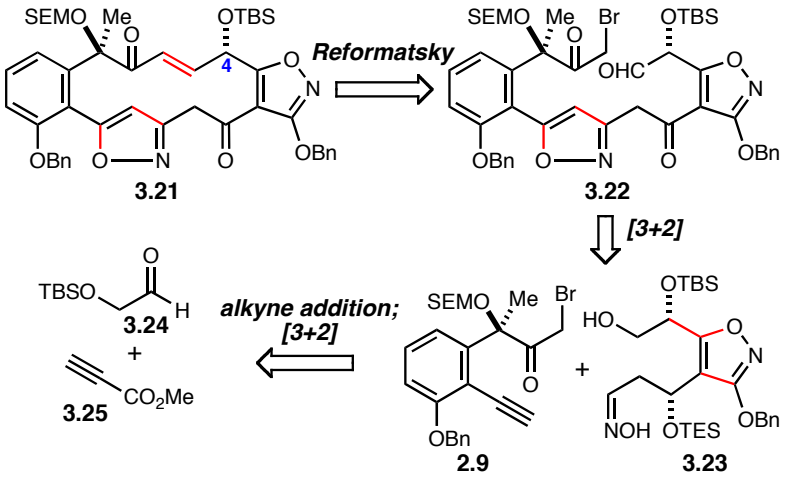

## IV. Synthesis of a C4-Oxygenated Macrocycle

An alternative reaction sequence to that used for the synthesis of macrocycle **2.3** was proposed for the oxygenated macrocycle **3.21**. This decision was based primarily on reasons of practicality, since the previous route to macrocycle **2.3** required the isolation and individual throughput of secondary carbinol diastereomers following Reformatsky coupling. To obviate this requirement, we proposed the use of an intermolecular nitrile-oxide cycloaddition to couple fragments **2.9** and **3.23**. This would be followed by a Re-

[121] The B3LYP hybrid functional with the 6-31G* basis set was used. M. J. Frisch.; *et al.* Gaussian, Inc., Pittsburgh, PA, 2006.

formatsky macrocyclization[122] to produce a mixture of aldol adducts which could be dehydrated immediately. Fragment **3.23** would be synthesized in a largely analogous manner to that of fragment **2.23**, with the exception being an asymmetric acetylide addition used to set the C4-stereocenter.

**Scheme 3.4** Synthesis plan to C4-oxygenated macrocycle **3.21**.




The synthesis of oxime **3.23** commenced via the asymmetric zinc acetylide addition to known aldehyde **3.24** in good yield and excellent enantioselectivity.[123,124,125] Noteably, this reaction fails if both aldehyde **3.24** and methyl propiolate **3.25** are added at

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[122] (a) Vedejs, E.; Duncan, S. M. *J. Org. Chem.* **2000**, *65*, 6073-6081. (b) Hong, Z.; Xu, X. *Tet. Lett.* **2003**, *44*, 489-491. (c) Nagamitsu, T.; Takano, D.; Fukuda, T.; Otoguro, K.; Kuwajima, I.; Harigaya, Y.; Omura, S. *Org. Lett.* **2004**, *6*, 1865-1867. (d) Nagamitsu, T.; Takano, D.; Marumoto, K.; Fukuda, T.; Furuya, K.; Otoguro, K.; Takeda, K.; Kuwajima, I.; Harigaya, Y.; Omura, S. *J. Org. Chem.* **2007**, *72*, 2744-2756.

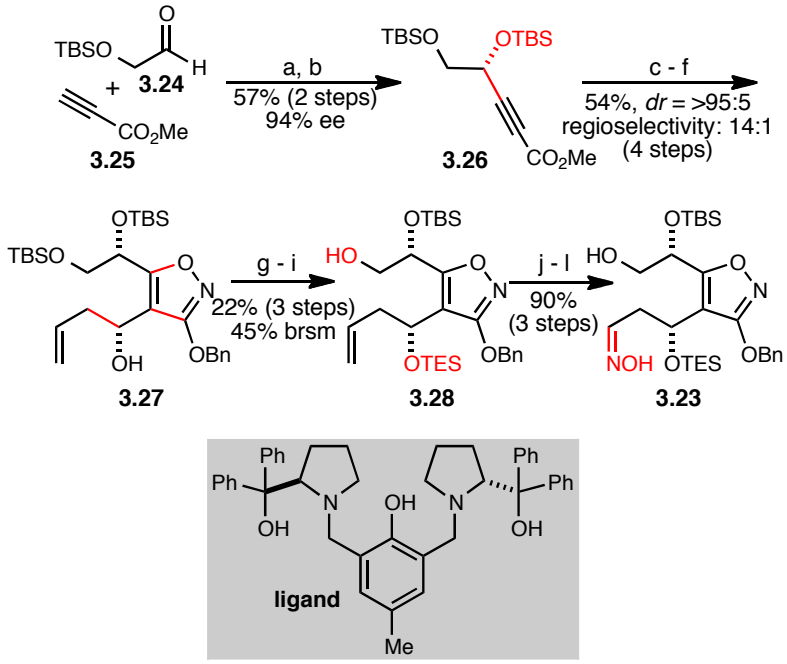
[123] (a) Trost, B. M.; Weiss, A. H.; von Wangelin, A. J. *J. Am. Chem. Soc.* **2006**, *128*, 8-9. (b) Trost, B. M.; Weiss, A. H. *Org. Lett.* **2006**, *8*, 4461-4464.

[124] The TES-protected derivative of aldehyde **3.24** is an equally competent coupling partner in this reaction, and would have resulted in a more efficient fragment synthesis overall. Unfortunately, we could not TBS-protect the secondary carbinol at C4 without silyl scrambling.

[125] Use of Carreira methodology was considered for this addition since a literature report shows the successful application on a similar aldehyde to that in Scheme 3.5. However the use of a superstoichiometric quantity of ligand deemed this method inferior to that described by Trost and co-workers. For an example of the Carreira method being used in this addition, see: Watanabe, H.; Mori, N.; Itoh, D.; Kitahara, T., Mori, K. *Angew. Chem. Int. Ed.* **2007**, *46*, 1512-1516.

the beginning of the reaction as is the standard protocol, due to aldehyde dimerization. Accordingly, slow addition of aldehyde to the reaction mixture is imperative. Protection of the secondary alcohol, followed by nitrile-oxide cycloaddition[126] and ester functionalization[127] produced **3.23** in 7 steps. Lastly, a three-step procedure was performed to produce the requisite oxime function for the eventual [3+2] fragment coupling reaction.

**Scheme 3.5** Synthesis of oxime **3.23**.




Reagents and conditions: (a) $Me_2Zn$, 10 mol % **ligand**, PhMe, –15 °C; (b) TBSCl, imidazole, DMF, 0 °C; 57% (2 steps), 94% ee; (c) NCS, $KHCO_3$, BnOCHNOH, EtOAc; (d) DIBAl-H, toluene, –78 °C; (e) $SO_3$•pyr., DIPEA, $CH_2Cl_2$, DMSO, 0 °C; (f) (+)-$IPC_2$Ballyl, $Et_2O$, pentane, –78 °C; 54% (4 steps), *dr* = >95:5, regioselectivity = >14:1; (g) HF•pyr., pyr., THF, rt; (h) TESCl, imidazole, DMF, 0 °C; (i) AcOH, MeOH, 0 °C to rt; 22% (3 steps, 45% brsm; (j) $OsO_4$, NMO, THF, acetone, pH 7 buffer, rt; $NaIO_4$, THF, pH 7 buffer, rt; $H_2NOH$•HCl, pyr., EtOH, 0 °C; 90% (3 steps).

Fragments **2.9** and **3.23** were coupled via nitrile-oxide cycloaddition in moderate yield (Scheme 3.6). The coupled material was next carried through the macrocyclization

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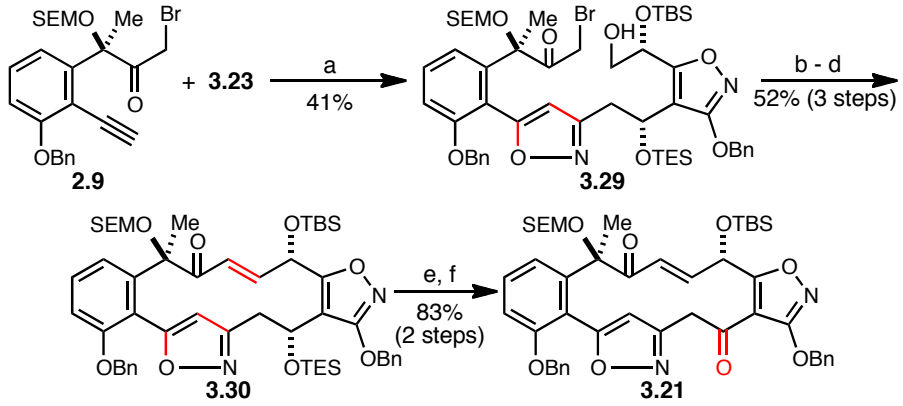
[126] Nitrile-oxide cycloaddition with the acetylide addition product (which does not have a silyl group on the secondary carbinol) proceeds with a lower ratio of regioisomers (6:1 vs. 14:1).

in good yield over the two steps. The inconsequential mixture of diastereomers was then dehydrated, and the intermediate macrocycle was elaborated to **3.21** in similar fashion to that established previously (*vide supra*). Notably, spectral comparison of **2.3** and the current macrocycle **3.21** (Figure 3.4) showed remarkable homology, alleviating our concerns that the overall conformation of the macrocycle might be perturbed by the NHBoc/OTBS substitution.

**Scheme 3.6** Synthesis of elaborated macrocycle **3.21**.




Reagents and conditions: (a) NCS, pyr., DIPEA, $CHCl_3$, rt to 60 °C; 41%; (b) DMP, $CH_2Cl_2$, rt; (c) $SmI_2$, THF, –78 °C; (d) Martin sulfurane, $CH_2Cl_2$, –78 °C to –20 °C; 52% (3 steps); (e) CSA, MeOH, $CH_2Cl_2$, 0 °C; (f) DMP, $CH_2Cl_2$, rt; 83% (2 steps).

[127] (a) Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1987**, *52*, 320-322. (b) Brown, H. C.; Bhat, K.

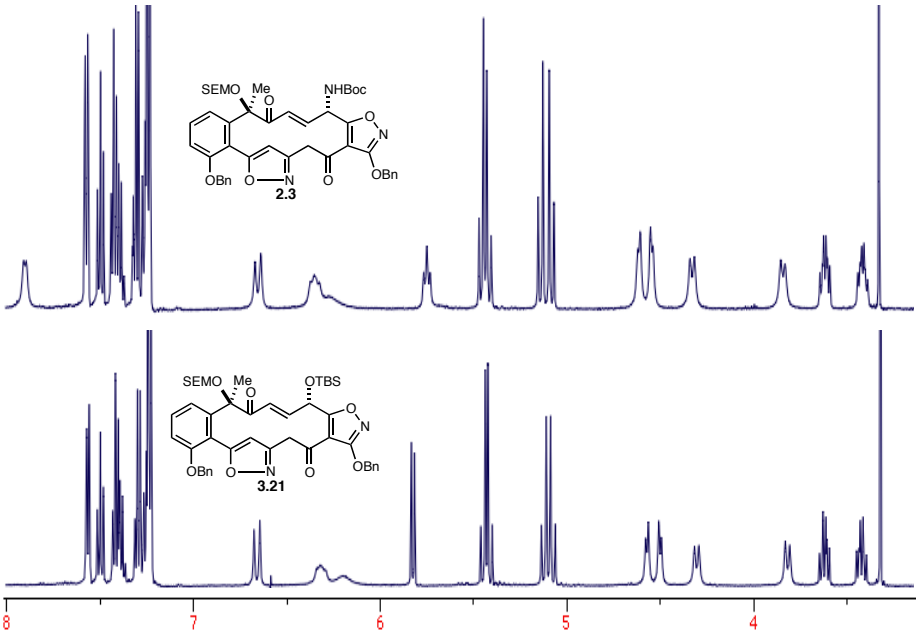



**Figure 3.4** $^{1}$H NMR spectral comparison of macrocycle **2.3** (upper) and macrocycle **3.21** (lower) in $d_6$-DMSO.

### V. Transannular Michael Reaction with a γ-Silyloxy Enone

Upon the synthesis of macrocycle **3.21**, we looked to execute the key reactions of our synthesis plan. Accordingly, macrocycle **3.21** was subjected to the previously established conditions for the transannular Michael addition, which employed the use of $Cu(OAc)_2 \bullet H_2O$ in methanol as solvent. Unbelievably, this reaction proceeded with the complete opposite sense of diastereoinduction, producing **3.31** as a sole detectable diastereomer (Scheme 3.7).[128] While the C12a-stereocenter is inconsequential, the C4a-stereocenter is now incorrect, eliminating the possibility of proceeding with **3.31** in the synthesis toward

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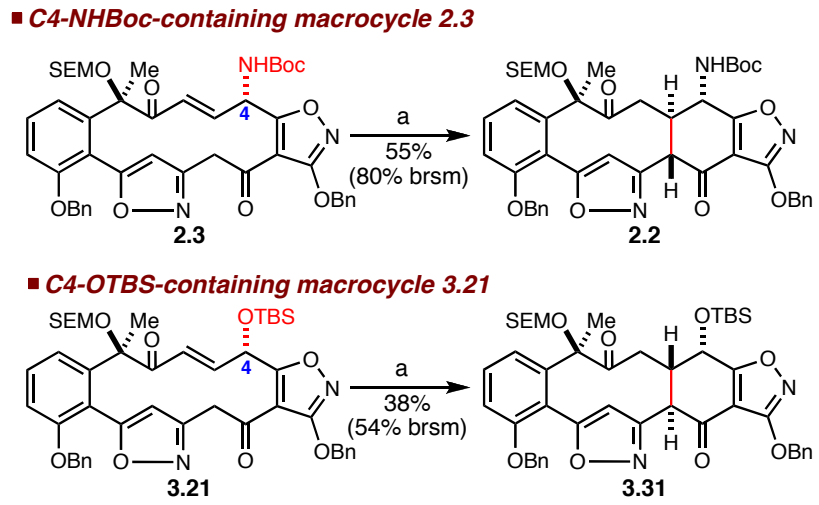
S.; Randad, R. S. *J. Org. Chem.* **1989**, *54*, 1570-1576.

[128] This reaction was less efficient compared to the reaction with the NHBoc-containing macrocycle **2.3**. The decreased efficiency is attributed to the reduced rate of reaction, which allowed the oxidative decomposition pathway to decompose the transannular Michael product to a greater extent.

tetracycline. In order to further understand the factors involved in this unexpected stereochemical outcome, we deprotected the C4-TBS group, and subjected the macrocycle to the same conditions. Yet, this too resulted in the exclusive formation of the incorrect C4a-stereocenter.

**Scheme 3.7** Transannular Michael additions yield divergent stereochemical outcomes.

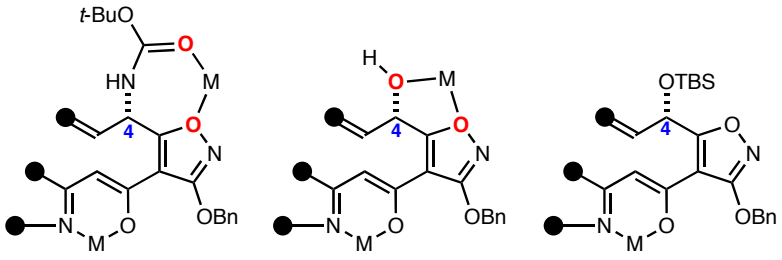



Reagents and conditions: (a) $Cu(OAc)_2 \cdot H_2O$, MeOH; see yield in equation.

It was initially believed that the divergence in diastereoselectivity could be attributed to chelation between the C4-substituent and the proximal isoxazole oxygen atom (**3.32**, Figure 3.5). This is feasible with an NHBoc group[129] but is uncommon with a TBS-protecting group unless special conditions are employed.[130] Thus, with the TBS-protected hydroxyl at C4, we may not have been able to access the macrocyclic enolate conformer needed to obtain the desired diastereomer. While the Michael reaction with a free hydroxyl at C4 is equally selective for the undesired diastereomer, this is not readily

[129] (a) Våbenø, J.; Brisander, M.; Lejon, T.; Luthman, K. *J. Org. Chem.* **2002**, *67*, 9186-9191. (b) Wang, D.-H.; Hao, X.-S.; Wu, D.-F.; Yu, J.-Q. *Org. Lett.* **2006**, *8*, 3387-3390.

comparable to the NHBoc example since it may not chelate as effectively. Also relevant to this discussion is the possibility that another mechanism of conformational perturbation is at play that does not involve chelation.[131] Specifically, it is possible that methanol acts as a stabilizing H-bond donor, bridging both the isoxazole and C4-oxygen atoms. If present within the system, this H-bond would perform a similar role compared to the metal-dependant chelation pathway outlined above.




**3.32** **3.33** **3.34**

**Figure 3.5** Possible modes of chelation with various substituents at C4. No chelation is feasible with **3.34** under the conditions used for the Michael reaction.

At this juncture, it was decided that the best course of action was to outline the system under which reaction was operating in order to more fully appreciate the perturbation induced by the C4-substituent (Scheme 3.8). In the originally proposed conformation, **3.35**, both the methyl group and NHBoc group are pseudoequatorial, which was considered the preferred conformation based upon dipole- and steric-based principles. Yet, with macrocycle **3.21**, another major conformation is being accessed in the transition state that places both the bulky TBS-protected alcohol and C6-methyl group pseudoaxial. Conformer **3.36** is most likely the ground state from which the transition state is emanat-

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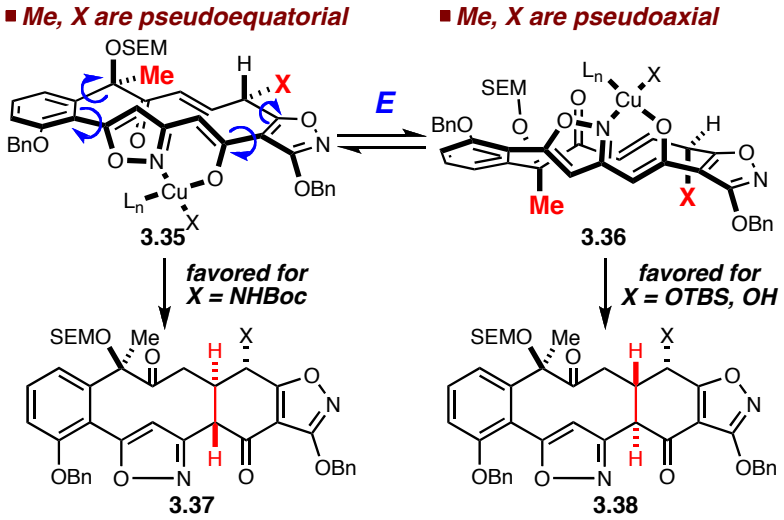
[130] (a) Evans, D. A.; Allison, B. D.; Yang, M. G.; Masse, C. E. *J. Am. Chem. Soc.* **2001**, *123*, 10840-10852. (b) Stanton, G. R.; Johnson, C. N.; Walsh, P. J. *J. Am. Chem. Soc.* **2010**, *132*, 4399-4408.

ing, however we had no further insight to support this claim. Therefore, we turned to computational chemistry to not only gain further understanding of the current system, but to search for an alternative path forward once again.

**Scheme 3.8** Interplay of two conformations may be responsible for the divergent stereochemical outcomes of macrocycles **2.3** and **3.21**.




## VI. The C4-C4a Stereochemical Relationship

Small perturbations may induce profound effects when stereochemical interplay within the system is not completely understood. In this instance, our solution for the C12a-hydroxylation reaction had introduced a problem with the Michael addition, forcing us to once-again reevaluate the influence of the C4-substituent. In order to tackle this challenge, we chose to computationally interrogate the conformational profile of macrocyclic enolates formed during the various transannular Michael additions executed to this point. The purpose of this exercise was to gain quantitative insight into the ground state conformations of these enolates, which may be used to guide our decision-making as we

[131] The feasibility of chelation understandably has been questioned since the reaction is conducted in a protic medium.

moved forward with the synthesis. While transition state computations would have been superior at this juncture, such a study was not feasible when time considerations were taken into account.

Ground state computations were performed using truncated forms of the macrocyclic enolates under consideration. An initial Monte Carlo conformational search was performed using Spartan 2004,[100] followed by refinement with DFT using Gaussian 2006.[132] The coordination sphere surrounding copper was assigned as a $\kappa^2$-acetate ligand and a bridging methanol ligand for reasons that will become apparent when the mechanism of the Michael reaction is formally addressed (*vide infra*).

We began the study by looking at the conformational profile of the C4-NHBoc macrocyclic enolate **3.39** in order to determine whether our initial assumptions were valid (Scheme 3.9). Encouragingly, favored enolate **3.39** places the –OMOM group anti to the ketone carbonyl oxygen and the NHBoc group in the pseudoequatorial position as we predicted at the outset of the project. If chelation or H-bonding is relevant in the Michael addition, it is likely that this conformer would be favored to an even greater extent, since the NHBoc group is nearly coplanar with the isoxazole oxygen atom. Based upon the stereochemical outcome of the Michael reaction with the corresponding macrocycle **2.3**, we can conclude that the low energy ground state most likely proceeds to the low energy selectivity determining transition state.

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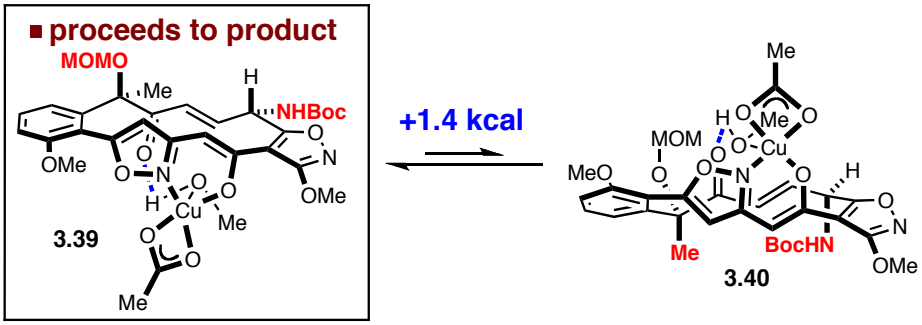
[132] The B3LYP hybrid functional with the 6-31G* (for H, C, O, and N) and MDF10 (for Cu) basis sets were used on truncated derivatives of the macrocycles under scrutiny. M. J. Frisch.; *et al.* Gaussian, Inc., Pittsburgh, PA, 2006. See the supporting information for complete details.

**Scheme 3.9** Equilibrium between conformers **3.39** and **3.40** derived from C4-NHBoc macrocycle **2.3**.[132]



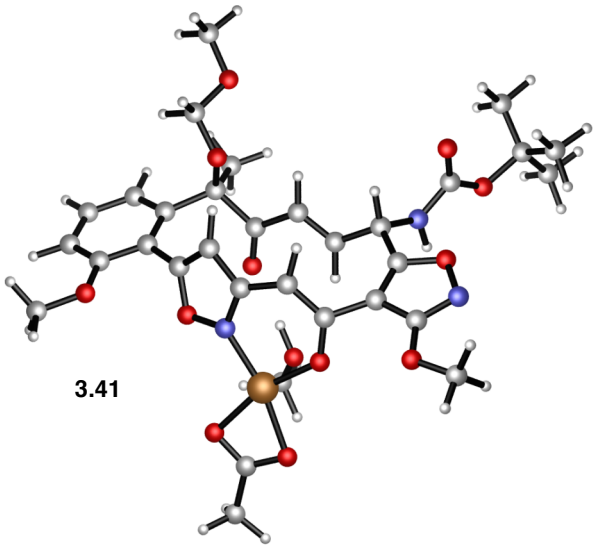
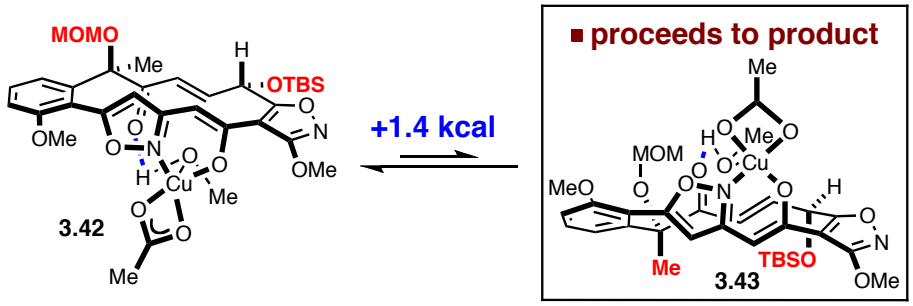




**Figure 3.6** Minimized structure of the low energy ground state **3.39**.[132]

When enolate conformers of macrocycle **3.21** were computed, we discovered a conformational profile that was remarkably similar to the NHBoc-derivative (Scheme 3.10). Specifically, the bulky silyloxy substituent is placed in the pseudoequatorial position and the heteroatom substituents at C5a and C6 were oriented anti to one another in the favored ground state conformer. Yet in contrast to the NHBoc-containing example above, this is not the structure from which the favored selectivity determining transition state emanates. Rather, Michael addition from the unfavored conformer proceeds to the observed diastereomer (Figure 3.7). This conformer profile, coupled with the high di-

astereoselectivity obtained experimentally, suggests that a long-standing suspicion about the system was true; the Michael reaction is operating under Curtin-Hammett kinetics.[133]

**Scheme 3.10** Equilibrium between conformers **3.42** and **3.43** derived from C4-OTBS macrocycle **3.21**.[132]



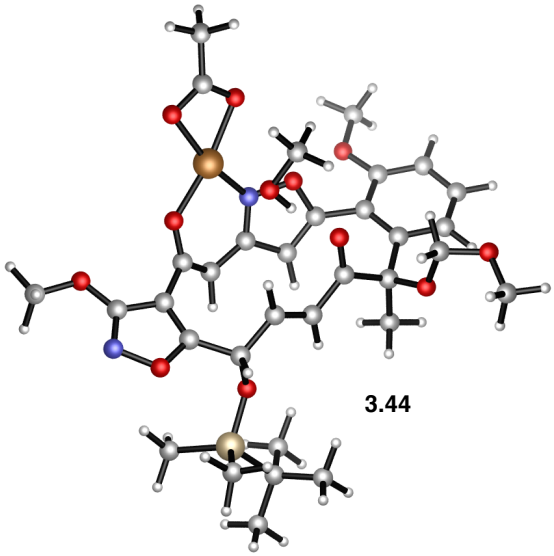




**Figure 3.7** Minimized structure of intermediate **3.43**, the ground state from which the transition state emenates.[132]

With the Curtin-Hammet kinetic system in mind, we closely examined conformer **3.43**, the conformer that proceeds to product in the Michael reaction, in an effort to glean insight into the transition state. Previously, it has been shown that γ-silyloxy-α,β-unsaturated carbonyl compounds undergo conjugate addition to yield products that arise

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[133] (a) Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83-134. (b) Seeman, J. I. *J. Chem. Ed.* **1986**, *1*, 42-48.

from a modified Felkin-Anh transition state model.[134] In the reported literature cases, the silyoxy substituent is oriented "inside", such that it is nearly coplanar with the acceptor enone. Indeed, in our macrocyclic setting, this appears to be dictating the outcome of the Michael addition. Transition state structure **3.45** (Figure 3.8) shows that the forming bond is antiperiplanar with the carbon-X bond in defiance of the model. Yet the structure that would emanate from conformer **3.43**, **3.46**, appears to be in a conformation that allows the X-type group to be nearly coplanar with the acceptor; the model predicts that this structure would be favored.

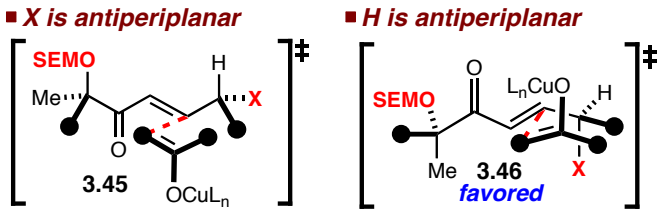


**Figure 3.8** Interaction of the forming transannular C-C bond and the antiperiplanar substituent may control the diastereoselection in the Michael reaction.

In an effort to develop a revised synthesis plan, we chose to compute the conformational profile of a third macrocycle (Scheme 3.11). This enolate, which is the C4-epimer of macrocycle **3.21**, was envisioned to facilitate the inversion of selectivity for the incorrect C4a-stereocenter. Encouragingly, ground state computations revealed the overwhelming preference for conformer **3.47**, which places both protected hydroxyls at C4 and C6 in the pseudoaxial position. Since the computed relative energy value of 4.0 kcal/mol is significantly greater than the 1.4 kcal/mol value obtained in the other two

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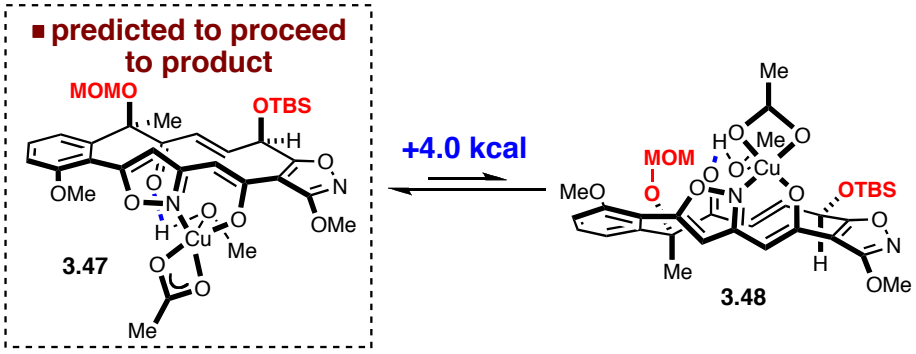
[134] (a) Hanessian, S.; Sumi, K. *Synthesis* **1991**, *12*, 1083-1089. (b) Yamamoto, Y.; Chounan, Y.; Nishii, S.; Ibuka, T.; Kitahara, H. *J. Am. Chem. Soc.* **1992**, *114*, 7652-7660. (c) Amigoni, S.; Schulz, J.; Martin, L.; Le Floc'h, Y. *Tet. Asymm.* **1997**, *8*, 1515-1518.

cases, the conformational preference suggests that the stereocenters at C4 and C6 are mutually reinforcing a single macrocyclic enolate conformation (Figure 3.9).

**Scheme 3.11** Equilibrium between conformers **3.47** and **3.48** derived from a C4-*epi*-OTBS macrocycle.[132]



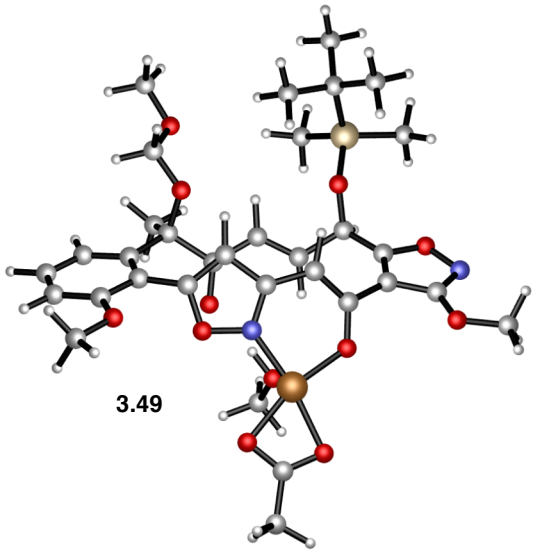
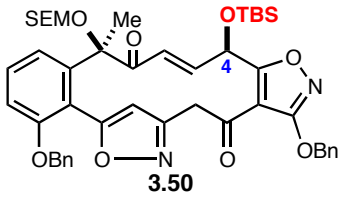




**Figure 3.9** Minimized structure of intermediate **3.47**.[132]

These energy values do not directly translate to the transition state barrier heights, since the putative reaction would likely also be a Curtin-Hammett scenario. Yet, favored enolate **3.47** is appropriately configured for enolate addition under modified Felkin-Anh control, the governing model to which we previously attributed the observed selectivity. If the relative energy values for enolate conformers **3.47** and **3.48** were reversed, it would

have been difficult to justify the synthesis of this new macrocyclic diastereomer, thus forcing us to consider a more significant route revision. With computational support for the synthesis of macrocycle **3.50**, we next looked to understand the implications of this new C4-stereocenter in the C12a-hydroxylation reaction.[135]




**3.50**

**Figure 3.10** Experimental and computational data justify the synthesis of macrocycle **3.50**.

## VII. A Model System for C12a-Hydroxylation

At this point, we had settled upon a path employing macrocycle **3.50** as a potential substrate to effect the formation of the C4a-C12a bond with the correct sense of diastereoinduction. Yet, the issue of C12a-oxidation had been left unaddressed. While we had hoped that an axial substituent would direct hydroxylation to the opposite face of the A-ring, this remained untested. Fortunately, the C4a-epi Michael product **3.31** served as an ideal model system for this transformation since the C6-stereocenter was remote, and the C4-OTBS substituent should exist in the axial position (Scheme 3.12).

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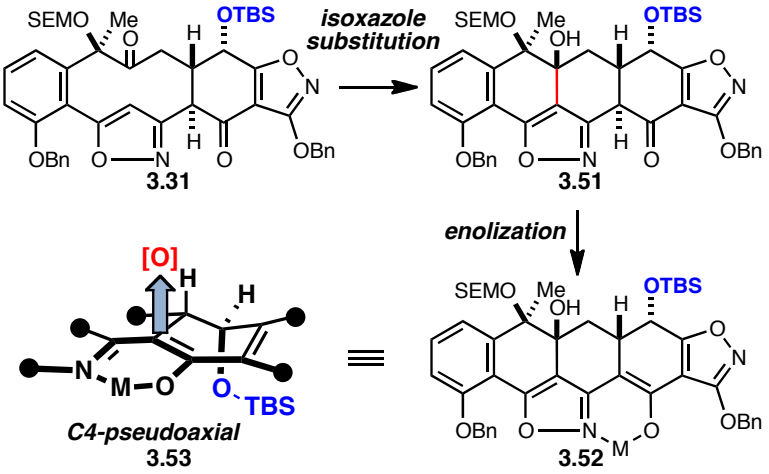
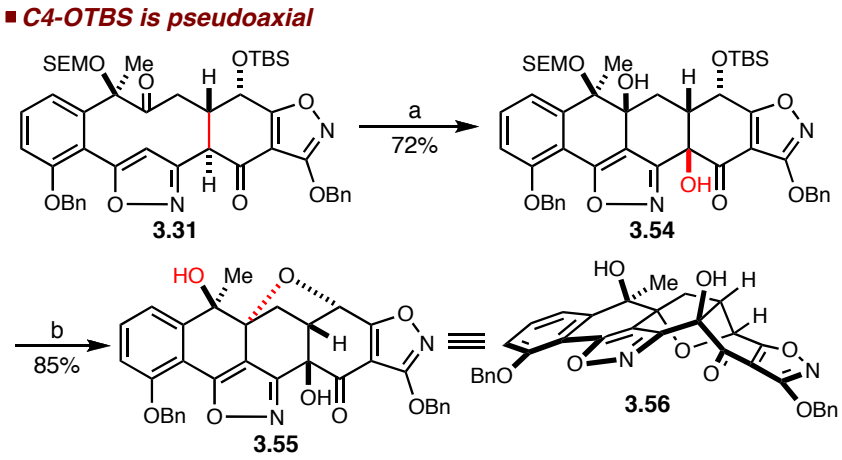
[135] This is another example of computational data helping direct the course of experimental research. Initially, I was not convinced that the synthesis of the C4-epimer was a reasonable endeavor since simple molecular models revealed that both the C4- and C6-protected hydroxyls would need to be pseudoaxial in the transition state. This conformation was considered difficult to access, and the complete conformational profile optomistically was thought to produce an unselective Michael reaction. Therefore, I was quite surprised to see the results of the conformational profile calculations. Without these data points, it is likely that I would not have pursued the synthesis of the new C4-macrocyclic diastereomer.

**Scheme 3.12** Michael product **3.31** may serve as a valuable model system for the C12a-hydroxylation reaction since the silyloxy group at C4 is pseudoaxial.




In the event, we subjected **3.31** to the previously established Ce(III)-mediated C12a-hydroxylation conditions. Encouragingly, these conditions afforded **3.54** in good yield and as a single diastereomer (Scheme 3.13). While nOe data strongly suggested the formation of a *cis* ring fusion, further functionalization served to reaffirm this assertion. Specifically, in order to deprotect intermediate **3.54**, we treated it with 4 *N* HCl, which resulted in not only the cleavage of the SEM and TBS protecting groups, but the cyclization of the C4-hydroxyl to the C5a position. This newly formed polycyclic structure further established that we had indeed synthesized a *cis* ring fusion, since the C12a-epimer would be incapable of undergoing cyclization. Additionally, this rigid system allowed the facile collection of nOe data which enabled rigorous assignment of relative stereochemical relationships (Figure 3.11).

**Scheme 3.13** Hydroxylation of **3.31**, an intermediate containing a pseudoaxial C4-OTBS substituent.




Reagents and conditions: (a) $CeCl_3 \cdot 7H_2O$, $O_2$, *i*-PrOH, rt; $Me_2S$, $CH_2Cl_2$, rt; 72%; (b) 4 *N* HCl, THF, rt; 85%.

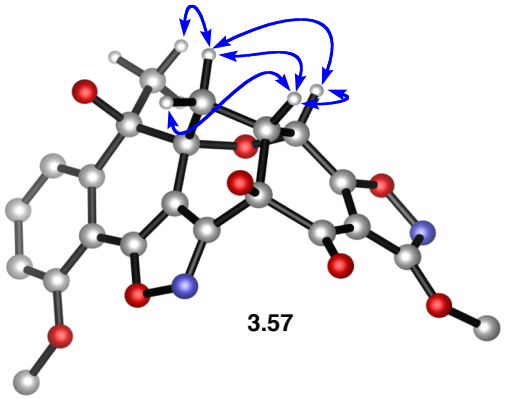
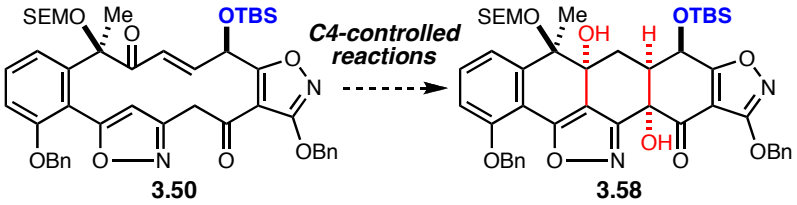



**Figure 3.11** Relevant nOe data (blue arrows) used to determine the stereochemistry of polycycle **3.56**. Molecular modeling was performed with truncated protecting groups, see reference [100] for details.

Collectively, the experimental data gathered from model system **3.31** coupled with the computational data concerning the Michael addition led us to the understanding that macrocycle **3.50** should facilitate both of our key steps, since the same C4-stereocenter is necessary (Scheme 3.14). This is in contrast to our previous synthesis plan employing **3.21**, which required an inversion at C4 between key steps, followed by a late-stage epimerization. A reasonable criticism entails the pursuit of macrocycle **3.50** when evidence strongly suggested that protection of macrocycle **3.21** with a carbonate at C4

would have yielded a substrate competent for chelation, and thus would have led to the correct Michael diastereomer. While this scenario is possible, the synthesis would then have required the same displacement and epimerization strategy originally envisioned for the OTBS-containing derivative. The newfound understanding that an epimeric C4-OTBS substituent (macrocycle **3.50**) may facilitate both reactions without the need for epimerization was deemed a superior overall approach. Thus, with the path forward now evident we embarked upon the synthesis of **3.50** with great optimism.

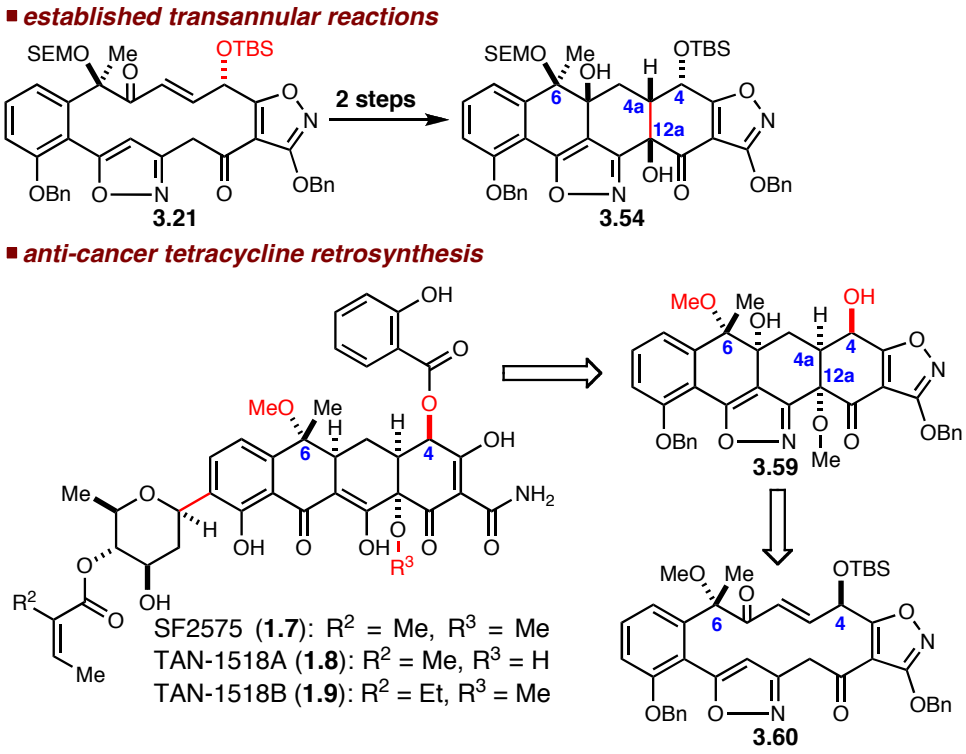
**Scheme 3.14** A single C4-stereocenter should control both the Michael addition and C12a-hydroxylation reaction.




## VIII. Implications for the Synthesis of Anti-Cancer Tetracyclines

While the transannular reactions employed to transform macrocycle **3.21** to **3.54** yielded material that was not useful as we attempted to synthesize tetracycline, it did open an interesting avenue for the synthesis of the anticancer tetracyclines **1.7** – **1.9** (Scheme 3.15). Specifically, since these natural products have an inverted C4- and C6-stereochemical relationship when compared with tetracycline, the result of the Michael and oxidation reactions discussed above is a compound that is enantiomeric to these natural products. Thus, using established reactions we can deconstruct **1.7** – **1.8** to intermediate **3.59**, which is a substrate that contains all of the requisite relative stereochemistry. Simply inverting the C4- and C6- stereocenters in macrocycle **3.21** should yield a viable synthesis of the natural configuration of these intriguing compounds.

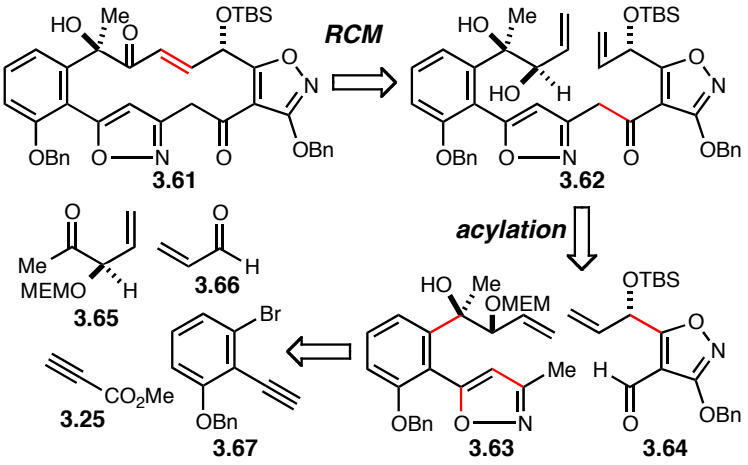
**Scheme 3.15** An approach to the anti-cancer tetracyclines utilizing the previously established transannular reactions.




## IX. An alternative Approach to a C4-OTBS Macrocycle

Prior to the synthesis of macrocycle **3.21** via an analogous route to that of the NHBoc-containing derivative **2.3**, we had considered an alternative and potentially more efficient approach (Scheme 3.16). Rather than performing an inter- or intramolecular nitrile-oxide cycloaddition, we envisioned using the intrinsic polarity of the C12a-position in a metalloenamine-like acylation event to couple fragments **3.63** and **3.64**. These fragments were envisioned to arise from a chelate-controlled addition of an aryl-lithium reagent to ketone **3.65** (western fragment) and zinc acetylide addition to acrolein (eastern fragment). The success of the approach hinged on the execution of a late-stage ring-closing metathesis reaction with substrate **3.62**. While this macrocyclization strategy undoubtedly is risky, the approach could enable the synthesis of macrocycle **3.61** in 12 longest-linear steps, a marked improvement over the existing macrocycle synthesis.

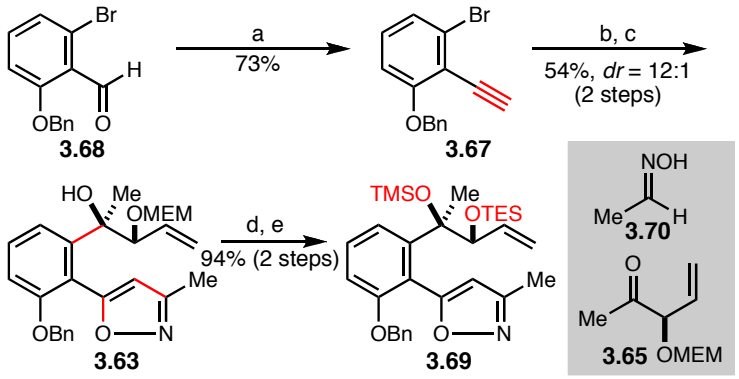
**Scheme 3.16** Retrosynthesis of macrocycle **3.61** employing a ring-closing metathesis reaction as the macrocyclization strategy.




Synthesis of the western fragment commenced via conversion of trisubstituted aromatic **3.68** to the terminal alkyne **3.67**. The alkyne was then utilized in an intermolecular nitrile-oxide cycloaddition with acetaldoxime (**3.70**). This intermediate was lithiated and coupled to known ketone **3.65**[136] in good yield and diastereoselection over the two steps. With the functionalized tertiary carbinol **3.63** in hand, we then performed a deprotection of the MEM ether and sequentially protected the remaining alcohol functions with silyl groups. Thus, **3.63** and **3.69** were considered viable fragments with which to couple to the eastern fragment.

[136] Ramachandran, P. V.; Liu, H.; Reddy, M. V. R.; Brown, H. C. *Org. Lett.* **2003**, *5*, 3755-3757.

**Scheme 3.17** Synthesis of the western fragment.




Reagents and conditions: (a) LDA, $TMSCHN_2$, THF, hexane, –78 °C to rt; 73%; (b) NCS, **3.70**, pyr., $NEt_3$, $CHCl_3$, 60 °C; (c) *t*-BuLi, $Et_2O$, THF, **3.65**, –78 °C; 54%, *dr* = 12:1 (2 steps); (d) HCl, MeOH, rt; (e) TESCl, TMSCl, imidazole, DMF, rt; 94% (2 steps).

Synthesis of the eastern fragment began with the asymmetric zinc acetyide addition to acrolein,[123] and the intermediate propargylic alcohol was protected as a TBS ether (Scheme 3.18). Unfortunately nitrile-oxide cycloaddition employing **3.71** failed since both the alkyne and alkene participated in the reaction. Even reduction of the alkynoate to the corresponding primary alcohol failed to yield a selective cycloaddition with the alkyne. Thus we were forced to "protect" the alkene via dihydroxylation,[137,138] yielding **3.72** after [3+2] cycloaddition. Conversion of the vicinal diols back to the olefin,[139] reduction of the ester, and oxidation yielded aldehyde **3.64**.

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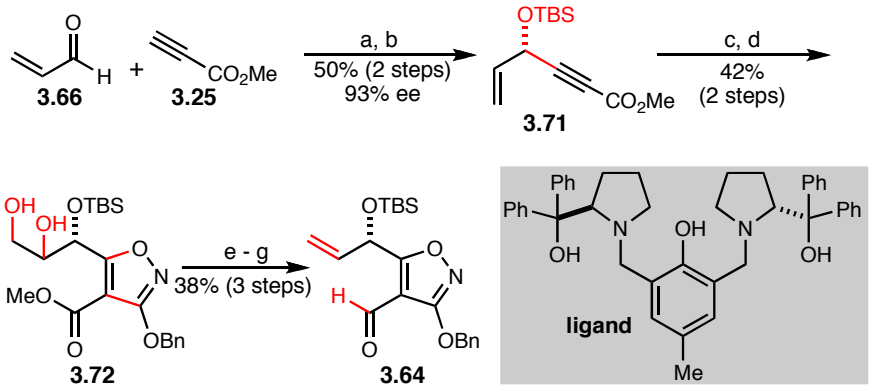
[137] (a) Plietker, B.; Niggemann, M.; Pollrich, A. *Org. Biomol. Chem.* **2004**, *2*, 1116-1124. (b) Plietker, B.; Niggemann, M. *J. Org. Chem.* **2005**, *70*, 2402-2405.

[138] The Plietker conditions employed in this transformation revealed the utility of the method. While $OsO_4$ failed to yield any dihydroxylated product, the ruthenium conditions yielded product exceedingly quickly (less than 30 minutes at room temperature). It is suggested that these conditions be employed more regularly in routine dihydroxylations due to the ease of operation, low reaction time, low catalyst loading, and relative low price and toxicity of ruthenium.

[139] (a) Liu, Z.; Classon, B. *J. Org. Chem.* **1990**, *55*, 4273-4275. (b) Luzzio, F. A.; Menes, M. E. *J. Org. Chem.* **1994**, *59*, 7267-7272. (c) Banda, G.; Chakravarthy, I. E. *Tet. Asymm.* **2006**, *17*, 1684-1687.

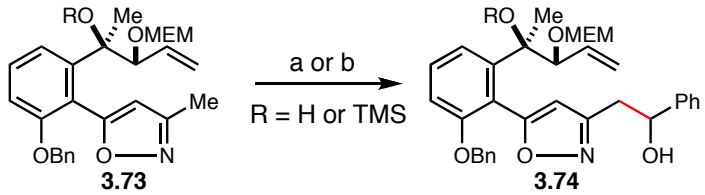
**Scheme 3.18** Synthesis of the eastern fragment.




Reagents and conditions: (a) $Me_2Zn$, 10 mol % **ligand**, PhMe, –5 °C; (b) TBSCl, imidazole, DMF, 0 °C; 50% (2 steps), 93% ee; (c) 0.5 mol % $RuCl_3{\cdot}H_2O$, 10 mol % $CeCl_3{\cdot}7H_2O$, $NaIO_4$, EtOAc, $CH_3CN$, $H_2O$, 0 °C; (d) NCS, $KHCO_3$, BnOCHNOH; 42% (2 steps); (e) $PPh_3$, $I_2$, imidazole, THF, 50 °C; (f) DIBAl-H, toluene, –78°C; (g) DMP, $CH_2Cl_2$, rt; 67% (3 steps).

Initially, coupling of fragment **3.73** with benzaldehyde as a model system with either the free tertiary carbinol or the tertiary TMS ether failed when LDA was used as base (Scheme 3.19).[140] However, using *t*-BuLi at low temperature in ether afforded the desired coupling reaction with 70% conversion. While this reaction could be optimized further, at this juncture the current conditions were considered sufficient to proceed with the coupling of **3.73** to aldehyde **3.64** such that the late-stage RCM could be explored.

**Scheme 3.19** Initial fragment coupling experiments.

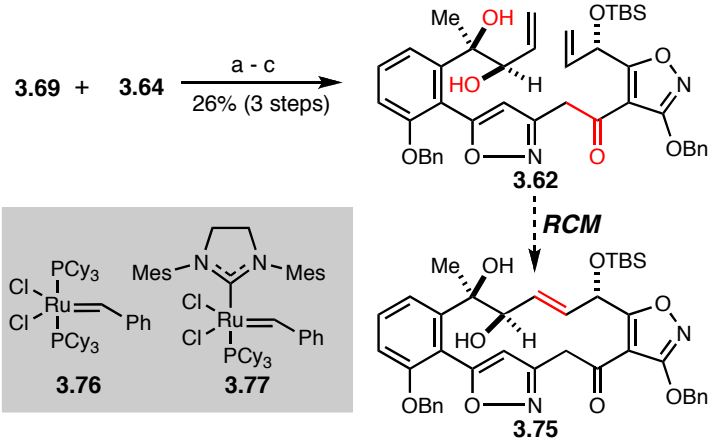



Reagents and conditions: (a) LDA then PhCHO, THF, –78°C; no reaction (R = H or TMS); (b) *t*-BuLi then PhCHO, $Et_2O$, –78°C; 70% NMR yield (R = TMS).

[140] Coupling reactions of this type are feasible using amide bases. For select examples see: (a) Alberola, A.; Calvo, L.; Rodriguez, T. R. *J. Heterocycl. Chem.* **1992**, *29*, 445-450. (b) Alberola, A.; Calvo, L.; Rod-

Employing the optimized conditions established from the coupling of **3.73** (R = TMS) and benzaldehyde, fragments **3.69** and **3.64** were coupled in an unoptimized 27% yield. Once coupled, the intermediate secondary carbinol was oxidized, and the silyl groups were removed under acidic conditions. The resulting vicinol diol **3.62** was then subjected to RCM conditions employing Grubbs I or Grubbs II catalysts. Unfortunately, no macrocyclized material was obtained in dichloromethane or benzene at room temperature or elevated temperature. This was surprising given previously successful macrocyclizations employing terminal olefins with allylic stereocenters.[141] Attempts to perform the reaction with both alcohol functions protected as their silyl ether also failed under the described conditions.

**Scheme 3.20** Fragment coupling and elaboration to the macrocyclic precursor.




Reagents and conditions: (a) *t*-BuLi, $Et_2O$, –78 °C; (b) DMP, $CH_2Cl_2$, rt; CSA, MeOH, 0 °C to rt; 26% (3 steps).

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riguez, T. R.; Sañudo, C. *J. Heterocycl. Chem.* **1995**, *32*, 537-541. (c) Fuentes, J. A.; Maestro, A.; Testera, A.; Báñez, J. M. *Tet. Asymm.* **2000**, *11*, 2565-2577.

[141] (a) Geng, X.; Danishefsky, S. J. *Org. Lett.* **2004**, *6*, 413-416. (b) Torssell, S.; Samfai, P. *Org. Biomol. Chem.* **2004**, *2*, 1643-1646. (c) Nicolaou, K. C.; Sun, Y.-P.; Guduru, R.; Banerji, B.; Chen, D. Y.-K. *J. Am. Chem. Soc.* **2008**, *130*, 3633-3644. (d) Hoveyda, A. H.; Lombardi, P. J.; O'Brien, R. V.; Zhugralin, A. R. *J. Am. Chem. Soc.* **2009**, *131*, 8378-8379.

This approach, while ultimately unsuccessful, paves the way for a macrocycle synthesis with dramatically improved step efficiency. At the time, we were more concerned with access to the macrocycle itself, and less concerned about the route that was used for this access, thus we moved on to the established approach (*vide supra*). It is strongly believed that with persistence and a more exhaustive catalyst screen, this route would indeed be fruitful.

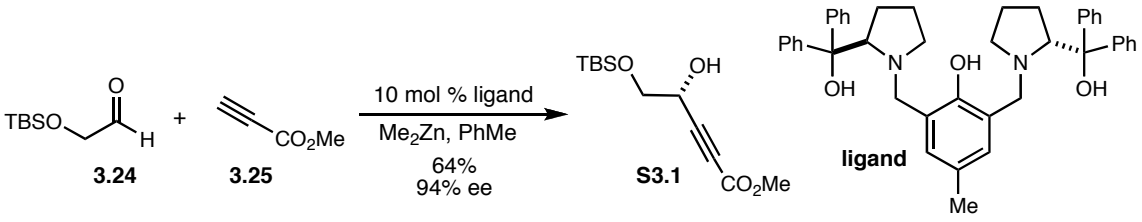
**X. Conclusion**

The results disclosed in this chapter reveal a possible solution to the C12a-hydroxylation problem presented in Chapter 2. This solution relies upon the incorporation of a pseudoaxial substituent in the C4-position. Importantly, computational data and chemical intuition were coupled to arrive at this conclusion, which was ultimately validated in a complex model system. Unfortunately, while the stereochemistry of C12a-hydroxylation has been satisfactorily addressed, the transannular Michael reaction was shown to be remarkly unpredictable since a minor perturbation to macrocycle **2.3** produced a divergent stereochemical outcome. Despite this unexpected result, computational data reveal a possible solution and further, both the Michael and C12a-hydroxylation reactions may now rely upon a single C4-stereocenter. If validated, this will represent a marked improvement over the existing synthesis plan. Chapter 4 will detail both the synthesis of this new macrocycle and the impact of the C4-stereocenter on the subsequent key steps.

# *Chapter 3*

## XI. Experimental Section

### A. Experimental Procedures




**(*R*)-methyl 5-(*tert*-butyldimethylsilyloxy)-4-hydroxypent-2-ynoate (S3.1).** To a solution of *R*-*R*-bis-prophenol **ligand**[142] (3.67 g, 5.75 mmol, 0.100 equiv.) in toluene (290 mL, 0.20 M wrt aldehyde **3.24**) at room temperature under an atmosphere of nitrogen, methyl propiolate **3.25** (15.3 mL, 173 mmol, 3.00 equiv.) was added rapidly via syringe. Next, dimethylzinc (144 mL of a 1.2 M solution in toluene, 173 mmol, 3.00 equiv.) was added rapidly via syringe to the solution (some gas evolution occurs). The reaction was then cooled to –15 °C, and alehyde **3.24** (10.0 g, 57.5 mmol, 1.00 equiv.) in toluene (10 mL,

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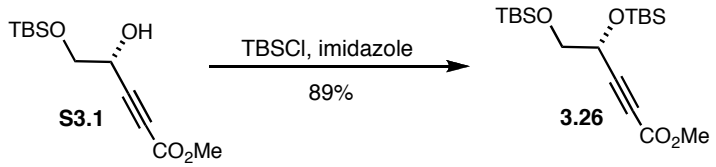
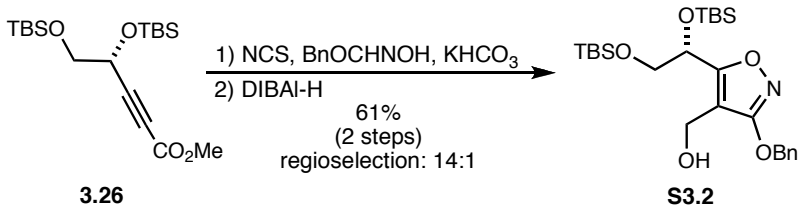
[142] (a) Trost, B. M.; Weiss, A. H.; von Wangelin, A. J. *J. Am. Chem. Soc.* **2006**, *128*, 8-9. (b) Trost, B. M.; Weiss, A. H. *Org. Lett.* **2006**, *8*, 4461-4464.

5.8 M) at room temperature was added directly to the cooled reaction via syringe pump over 36 h. The reaction was carefully quenched via addition of sat. $NH_4Cl$ (caution, gas evolution occurs) and extracted three times with $Et_2O$. The combined organic extracts were washed once with water, dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude material was purified via MPLC (5% → 20% EtOAc and hexanes) affording **S3.1** (9.46 g, 64% yield, 94% ee) as a slightly yellow liquid. $\boldsymbol{R_f}$ = 0.34 (6:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –13.6 (*c* 1.45, $CHCl_3$); **IR** (neat) 3435, 2955, 2930, 2858, 2242, 1721, 1436, 1255, 1125, 1048, 838; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 4.08 (dt, *J* = 6.5, 4.8 Hz, 1H), 3.39 (qd, *J* = 10.1, 5.0 Hz, 2H), 3.20 (s, 3H), 2.02 (d, *J* = 6.6 Hz, 1H), 0.86 (s, 9H), -0.05 (d, *J* = 6.7 Hz, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 153.58, 128.09, 127.89, 127.70, 86.42, 76.97, 66.27, 63.13, 52.01, 25.81, 18.31, -5.47, -5.53; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 259.1360; found: 259.1358 (ESI).




**(*R*)-methyl 4,5-bis(*tert*-butyldimethylsilyloxy)pent-2-ynoate (3.26).** To a solution of **S3.1** (9.30 g, 36.0 mmol, 1.00 equiv.) in DMF (90 mL, 0.40 M) at 0 °C under an atmosphere of nitrogen, imidazole (4.90 g, 72.0 mmol, 2.0 equiv.) was added in a single portion, followed TBSCl (5.97 g, 39.6 mmol, 1.10 equiv.) also in a single portion. The reaction was stirred for 4 h, upon which time it was quenched with water and stirred for 5 minutes. The resulting mixture was extracted three times with hexanes, and the combined or-

ganic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography (16:1 hexanes:EtOAc) affording **3.26** (11.9 g, 89%) as a colorless liquid. $R_f$ = 0.63 (10:1 hexanes:EtOAc); $[\alpha]_D$ = –24 (*c* 0.85, $CHCl_3$); **IR** (neat) 2955, 2930, 2859, 2241, 1723, 1435, 1254, 1135, 1109, 960, 835; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 4.45 (dd, *J* = 6.7, 5.4 Hz, 1H), 3.81 - 3.54 (m, 2H), 3.19 (s, 3H), 0.95 (d, *J* = 5.7 Hz, 8H), 0.32 – -0.08 (m, 12H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 153.46, 128.18, 128.08, 128.00, 127.89, 127.80, 127.70, 86.78, 77.24, 67.38, 64.79, 51.92, 25.90, 25.76, 18.37, 18.26, -4.76, -5.00, -5.37, -5.43; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 395.2044; found: 395.2058 (ESI).

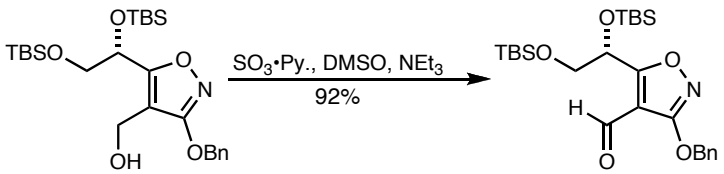



**3.26** **S3.2**

**(*S*)-(3-(benzyloxy)-5-(2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecan-5-yl)isoxazol-4-yl)methanol (S3.2).** To a solution of **3.26** (11.9 g, 31.9 mmol, 1.00 equiv.) in EtOAc (160 mL, 0.2 M) at room temperature exposed to air, BnOCHNOH (9.64 g, 63.8 mmol, 2.00 equiv.) was added, followed by the addition of $KHCO_3$ (31.9 g, 319 mmol, 10.0 equiv.) and NCS (8.52 g, 63.8 mmol, 2.00 equiv.). The flask was fitted with a reflux condensor, and the suspension was heated to 48 °C under an atmosphere of nitrogen for 12 h. The reaction was treated with an additional 1.00 equiv. of oxime and NCS every 12 h for a total 6 additions or 6 equiv. of each. The resulting cloudy and slightly yellow mixture was passed through celite, and the resulting pad of celite was washed with EtOAc.

After concentration of the solution *in vacuo*, the resulting residue was suspended in hexanes and passed through celite once again. Following this second filtration, the solution was concentrated *in vacuo* once more. The crude material was purified via MPLC (0% → 10% EtOAc and hexanes) affording the intermediate ester (12.9 g, 78% yield, 14:1 regioselectivity) as a slightly yellow liquid that was ca. 90% pure as determined by NMR.

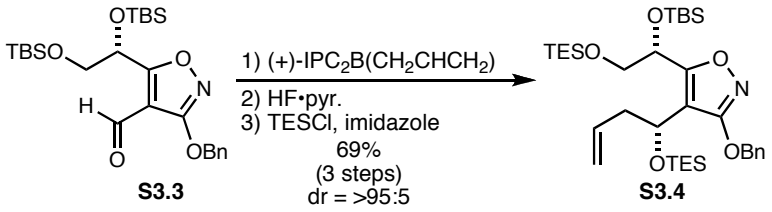
To a solution of the intermediate ester (12.9 g, 24.7 mmol, 1.00 equiv.) in toluene (124 mL, 0.20 M) at –78 °C under an atmosphere of argon, DIBAl-H (74.0 mL of a 1.0 M solution in hexane, 74.1 mmol, 3.00 equiv.) at –78 °C was added against the side of the flask over 15 minutes via cannula. The resulting slightly yellow solution was stirred at –78 °C for 2 h, upon which time it was carefully quenched with a 20% w/v solution of Rochelle's salt. The reaction was then warmed to room temperature while stirring vigorously for 12 h, upon which time the biphasic mixture was extracted three times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (10:1 hexanes:EtOAc) affording **S3.2** (9.54 g, 78%, 61% from **3.26**) as a clear liquid. $\boldsymbol{R_f}$ = 0.63 (5:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –16 (*c* 4.1, $CHCl_3$); **IR** (neat) 3446, 2954, 2930, 2858, 1646, 1512, 1464, 1362, 1257, 1131, 1006, 836; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.22 – 7.16 (m, 2H), 7.11 – 7.00 (m, 1H), 5.16 (s, 2H), 4.96 (t, *J* = 5.8 Hz, 1H), 4.64 – 4.38 (m, 2H), 3.95 – 3.75 (m, 2H), 2.49 (dq, *J* = 6.8, 2.5 Hz, 1H), 0.88 (d, *J* = 14.2 Hz, 18H), 0.18 – -0.17 (m, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 170.08, 169.46, 136.19, 128.50, 128.42, 128.32, 107.99, 71.68, 70.07, 66.94, 52.54, 25.93, 25.75, 18.42, 18.24, -5.14, -5.51, -5.61; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 516.2572; found: 516.2569 (ESI).




**S3.2** **S3.3**

**(*S*)-3-(benzyloxy)-5-(2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecan-5-yl)isoxazole-4-carbaldehyde (S3.3).** To a solution of **S3.2** (9.54 g, 19.3 mmol, 1.00 equiv.) in $CH_2Cl_2$ (48 mL, 0.40 M) at 0 °C under an atmosphere of nitrogen, DMSO (11 mL, 1.7 M) was added followed by DIPEA (13.2 mL, 77.2 mmol, 4.00 equiv.). To a second flask, DMSO (29 mL, 2.0 M wrt $SO_3$•pyr.) was added, followed by $SO_3$•pyr. (9.22 g, 57.8 mmol, 3.00 equiv.). This mixture was stirred for 5 minutes upon which time most solid had dissolved. Next, the $SO_3$•pyr. solution was added to the solution containing **S3.2** rapidly via syringe. The resulting clear and slightly brown mixture was stirred for one hour at 0 °C, upon which time the reaction was placed under reduced pressure, and the $CH_2Cl_2$ was removed *in vacuo* on a rotovap with the bath temperature set to 29 °C. The remaining solution was poured directly onto a silica gel column and purified via flash chromatography (15:1 hexanes:EtOAc) affording **S3.3** (8.75 g, 92%) as a clear liquid. $\boldsymbol{R_f}$ = 0.73 (10:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –16 (*c* 1.4, $CHCl_3$); **IR** (neat) 2955, 2930, 2858, 1697, 1610, 1509, 1464, 1362, 1257, 1115, 1005, 960, 834; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 9.87 (d, *J* = 1.1 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.06 (qd, *J* = 7.7, 3.9 Hz, 3H), 5.45 (t, *J* = 5.7 Hz, 1H), 5.21 – 4.99 (m, 2H), 3.89 (d, *J* = 5.8 Hz, 2H), 0.89 (d, *J* = 12.1 Hz, 18H), 0.16 – -0.13 (m, 12H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 182.41, 178.20, 169.78, 135.48, 128.55, 128.53, 128.42, 108.86, 72.16, 69.81, 66.37, 25.83, 25.68, 18.29, 18.20, -

5.13, -5.20, -5.50, -5.60; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 492.2596; found: 492.2597 (ESI).




**3-(benzyloxy)-5-((*S*)-8,8-diethyl-2,2,3,3-tetramethyl-4,7-dioxa-3,8-disiladecan-5-yl)-4-((*R*)-1-(triethyl-silyloxy)but-3-enyl)isoxazole (S3.4).** To a solution of (+)-$IPC_2B(CH_2CHCH_2)$[143] (23 mL of a 1.0 M solution in pentane, 23 mmol, 1.30 equiv.) in ether (40 mL, 0.58 M wrt reagent) at –78 °C under an atmosphere of nitrogen, **S3.3** in $Et_2O$ (89 mL, 0.20 M) was added along the side of the flask via cannula while maintaining an internal temperature of < –72 °C. The resulting solution was stirred for 45 minutes, upon which time it was warmed directly to 0 °C, and a premixed solution of 2:1 2 *N* NaOH : 30% aq. $H_2O_2$ (89 mL) at room temperature was added portionwise. The reaction was then stirred vigorously for 30 miutes at 0 °C, upon which time the cooling bath was removed, and the cloudy mixture was stirred for an additional 1.5 h. The resulting solution was extracted three times with hexanes. The combined organic extracts were then dried with $Na_2SO_4$ concentrated *in vacuo*. The crude liquid was purified via flash chromatography on silica gel (pure hexanes → 15:1 hexanes:EtOAc) affording the intermediate ho-

[143] (a) Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1987**, *52*, 320-322. (b) Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1989**, *54*, 1570-1576.

moallylic alcohol (9.12 g, 96%, >95:5 dr) as a colorless liquid that was ca. 90% pure by NMR.

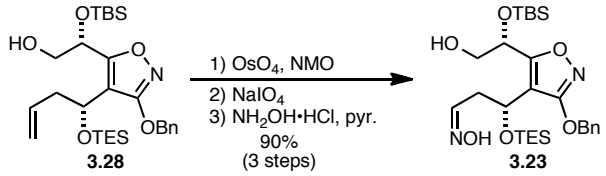
To a solution of 5:2:1 THF:pyr.:HF•pyr. (68.4 mL, 4 ml solution/mmol sm) at room temperature in a plastic bottle exposed to air, the homoallylic alcohol (9.12 g, 17.1 mmol) in THF (86 mL, 0.20 M) was added rapidly. The reaction was stirred for 45 minutes at room temperature, upon which time it was quenched with sat. $NaHCO_3$ (caution, gas evolution), and stirred vigorously for 12 h. The resulting mixture was extracted three times with $CH_2Cl_2$, and the combined organic extracts were dried with $Na_2SO_4$, and concentrated *in vacuo*. The resulting liquid was purified via flash chromatography on silica gel (2:1 hexanes:EtOAc) affording the intermediate diol (5.25 g, 73%) as a slightly pink liquid.

To a solution of the intermediate diol (5.05 g, 12.0 mmol, 1.00 equiv.) in DMF (60 mL) at room temperature under an atmosphere of nitrogen, imidazole (4.08 g, 60.0 mmol, 5.00 equiv.) was added, followed by TESCl (6.04 mL, 36.0 mmol, 3.00 equiv.) over 3 minutes. The resulting clear solution was stirred at room temperature for 1 hour, upon which time it was cooled to 0 °C, quenched with $H_2O$, and extracted three times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (20:1 hexanes:EtOAc) affording **S3.4** (3.21 g, 99%) as a colorless liquid. Yield for the three steps: 69%. $\boldsymbol{R_f}$ = 0.61 (10:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –6.1 (*c* 0.80, $CHCl_3$); **IR** (neat) 2955, 2878, 1641, 1509, 1460, 1414, 1361, 1251, 1128, 1089, 1006, 837, 742; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 3.9 Hz,

1H), 6.03 – 5.81 (m, 1H), 5.32 (dd, *J* = 7.9, 4.1 Hz, 1H), 5.22 (d, *J* = 1.9 Hz, 2H), 5.13 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.06 (d, 1H), 4.97 (dd, *J* = 7.3, 6.0 Hz, 1H), 4.04 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.94 (dd, *J* = 10.0, 4.1 Hz, 1H), 2.94 – 2.77 (m, 1H), 2.73 – 2.61 (m, 1H), 1.11 – 0.89 (m, 36H), 0.72 – 0.52 (m, 18H), 0.20 (d, *J* = 19.5 Hz, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 169.65, 167.97, 136.48, 134.80, 128.46, 128.30, 117.57, 109.33, 71.58, 70.12, 66.91, 65.60, 43.07, 25.98, 25.95, 18.43, 6.98, 6.89, 6.72, 5.16, 5.13, 4.56, -4.33, -4.63; **HRMS**: Exact mass calcd for [(M+Na$^+$)]: 648.3930; found: 648.3967 (ESI).


**(*S*)-2-(3-(benzyloxy)-4-((*R*)-1-(triethylsilyloxy)but-3-enyl)isoxazol-5-yl)-2-(*tert*-butyl-dimethylsilyloxy)-ethanol (3.28).** To a solution of **S3.4** (6.31 g, 9.74 mmol, 1.00 equiv.) in methanol (49 mL, 0.20 M) at 0 °C under a balloon of nitrogen, AcOH (0.560 mL, 9.74 mmol, 1.00 equiv.) was added dropwise. The resulting slightly turbid solution was stirred for 26 h during which time the cooling bath was allowed to expire. The reaction was quenched with sat. $NaHCO_3$ and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (8:1 hexanes:EtOAc → 1:1 hexanes:EtOAc, affording **3.28** (1.55 g, 30%) as a colorless liquid and starting material **S3.4** (3.26 g, 52%). $R_f$ = 0.17 (10:1 hexanes:EtOAc); $[\alpha]_D$ = –12 (*c* 0.1.4, $CHCl_3$); **IR** (neat) 3451, 2955, 2934, 2878, 2859, 1641, 1510, 1462, 1414, 1360, 1255, 1082, 1005, 951,

837, 779, 743, 696; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.08 (t, *J* = 7.1 Hz, 2H), 7.03 (d, *J* = 7.5 Hz, 1H), 5.83 (tdd, *J* = 10.0, 7.1, 2.7 Hz, 1H), 5.24 (td, *J* = 4.8, 2.3 Hz, 1H), 5.20 (d, *J* = 1.6 Hz, 2H), 5.08 (dt, *J* = 17.1, 1.9 Hz, 1H), 5.02 (dt, *J* = 10.4, 1.8 Hz, 1H), 4.88 (td, *J* = 6.6, 2.2 Hz, 1H), 3.93 – 3.72 (m, 2H), 2.83 – 2.52 (m, 2H), 1.99 – 1.79 (m, 1H), 1.14 – 0.81 (m, 18H), 0.56 (q, *J* = 7.7 Hz, 6H), 0.09 (q, *J* = 1.4 Hz, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 169.41, 167.92, 136.33, 134.33, 128.49, 128.38, 128.32, 117.80, 109.32, 71.68, 69.63, 66.27, 65.49, 42.87, 25.83, 18.31, 6.89, 5.00, -4.68, -4.85; **HRMS**: Exact mass calcd for [(M+Na$^+$)]: 556.2885; found: 556.2878 (ESI).



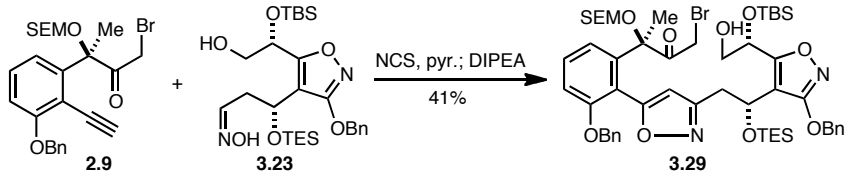

**(*R*)-3-(3-(benzyloxy)-5-((*S*)-1-(*tert*-butyldimethylsilyloxy)-2-hydroxyethyl)isoxazol-4-yl)-3-(triethylsilyloxy)propanal oxime (3.23).** To a solution of **3.28** (586 mg, 1.10 mmol, 1.00 equiv.) in 1:1:1 acetone:pH 7 phosphate buffer:THF (11 mL total, 0.10 M) at room temperature exposed to air, NMO (193 mg, 1.65 mmol, 1.50 equiv.) was added, followed by $OsO_4$ (550 μL of a 2.5 wt% solution in water, 0.050 equiv.). The reaction was stirred for 2 h at room temperature, upon which time it was cooled to 0 °C and a sat. $NaHCO_3$ solution (10 mL) containing 100 mg $NaHSO_3$ was added. The reaction quickly turned brown after this addition. The cooling bath was removed, and the reaction was stirred for 5 minutes. The resulting mixture was diluted with $H_2O$ (10 mL) and extracted

three times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* to afford a brown foam.

The intermediate diol was immediately dissolved in a 3:1 mixture of THF:pH 7 phosphate buffer (11.0 mL total, 0.10 M) at room temperature exposed to air, and $NaIO_4$ (941 mg, 4.40 mmol, 4.00 equiv.) was added in a single portion. The reaction soon became cloudy upon this addition. After stirring for 30 minutes at room temperature, the reaction was diluted with $H_2O$ and extracted three times with $CH_2Cl_2$. The combined organic extracts were washed once with brine, dried with $Na_2SO_4$, and concentrated *in vacuo* affording a brown foam.

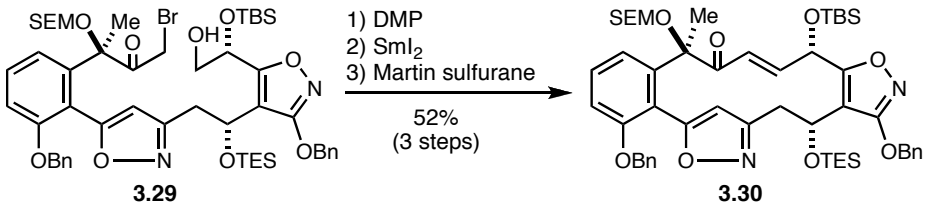
The intermediate aldehyde was dissolved in absolute ethanol (11.0 mL, 0.10 M) and cooled to 0 °C under an atmosphere of nitrogen. Next, pyridine (1.1 mL, 1.0 M wrt **3.28**) was added followed by hydroxylamine hydrochloride (304 mg, 4.40 mmol, 4.00 equiv.). The resulting solution was stirred for one hour, upon which time the reaction was warmed to room temperature and stirred for an additional 30 minutes. The reaction was quenched at 0 °C with sat. $NH_4Cl$. The resulting mixture was then diluted with $H_2O$ and extracted three times with $Et_2O$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The resulting residue was purified via flash chromatography on silica gel (3:1 hexanes:EtOAc) affording **3.23** (548 mg, 90%) as a white foam and a ca. 1:1 mixture of *E* and *Z* oxime isomers. Note: Characterized as a ca. 1:1 mixture of *E* and *Z* oxime isomers. $\boldsymbol{R_f}$ = 0.55 (2:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –6.0 (*c* 0.45, $CHCl_3$); **IR** (neat) 3339, 2956, 2879, 1509, 1459, 1363, 1259, 1087, 1005, 949, 838; **$^1$H NMR** (600 MHz, $C_6D_6$) δ 8.90 (s, 1H), 8.39 (s, 1H), 7.44 (t, *J* = 6.1 Hz, 1H), 7.35 – 7.24 (m,

4H), 7.15 – 7.08 (m, 4H), 7.08 – 7.01 (m, 2H), 6.86 (t, *J* = 5.2 Hz, 1H), 5.22 (s, 4H), 5.22 – 5.13 (m, 6H), 5.09 (t, *J* = 6.6 Hz, 1H), 5.01 (t, *J* = 6.5 Hz, 1H), 3.91 – 3.72 (m, 4H), 3.15 (ddd, *J* = 15.7, 6.9, 5.2 Hz, 1H), 3.02 – 2.90 (m, 1H), 2.84 – 2.76 (m, 1H), 2.76 – 2.65 (m, 1H), 2.58 (s, 1H), 2.29 (s, 1H), 0.95 (d, *J* = 2.8 Hz, 18H), 0.90 (td, *J* = 8.0, 2.9 Hz, 18H), 0.55 (qd, *J* = 7.9, 2.3 Hz, 12H), 0.12 (dd, *J* = 4.3, 2.2 Hz, 12H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 169.54, 169.49, 167.94, 167.81, 148.16, 148.09, 136.28, 136.23, 128.52, 128.45, 128.39, 128.35, 109.05, 108.83, 71.83, 71.81, 69.48, 69.42, 66.09, 63.97, 62.88, 38.10, 34.04, 25.83, 18.32, 6.85, 4.95, 4.93, -4.69, -4.74, -4.85; **HRMS**: Exact mass calcd for [(M+Na$^+$)]: 573.2787; found: 573.2796 (ESI).




**(*R*)-3-(3-(benzyloxy)-2-(3-((*R*)-2-(3-(benzyloxy)-5-((*S*)-1-(*tert*-butyldimethylsilyloxy) -2-hydroxyethyl)-isoxazol-4-yl)-2-(triethylsilyloxy)ethyl)isoxazol-5-yl)phenyl)-1-bromo-3-((2-(trimethylsilyl)ethoxy)me-thoxy)butan-2-one (3.29).** To a solution of **2.9** (1.54 g, 3.06 mmol, 3.06 equiv.) and **3.23** (549 mg, 1.00 mmol, 1.00 equiv.) in $CHCl_3$ (20 mL, 0.050 M) at room temperature under an atmosphere of nitrogen, pyridine (0.404 mL, 5.00 mmol, 5.00 equiv.) was added, followed by NCS (140 mg, 1.05 mmol, 1.05 equiv.). The reaction was stirred at room temperature for 45 minutes, upon which time DIPEA (0.342 mL, 2.00 mmol, 2.00 equiv.) in chloroform (5.0 mL, 0.2 M) was added directly to the solution over 24 h via syringe pump. The resulting orange/yellow solution

was treated with 2 additional equiv. of DIPEA (neat) and heated to 60 °C for 20 h, upon which time the reaction was concentrated *in vacuo* directly and purified via MPLC (5% → 40% EtOAc and hexanes) affording **3.29** (430 mg, 41% yield) as a slightly yellow liquid. $R_f$ = 0.42 (3:1 hexanes:EtOAc); $[\alpha]_D$ = –6.7 (*c* 0.2.3, $CHCl_3$); **IR** (neat) 3433, 2954, 2879, 1740, 1612, 1577, 1511, 1454, 1274, 1250, 1067, 1005, 858, 837, 744, 696; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.34 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.14 – 7.00 (m, 8H), 6.98 – 6.90 (m, 2H), 6.52 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.14 (s, 1H), 5.43 (t, *J* = 7.2 Hz, 1H), 5.33 – 5.15 (m, 3H), 4.65 (s, 2H), 4.46 (q, 2H), 4.23 (q, 2H), 3.95 – 3.76 (m, 2H), 3.65 (td, *J* = 8.9, 7.3 Hz, 1H), 3.55 (dd, *J* = 14.7, 7.4 Hz, 1H), 3.42 (dd, *J* = 14.7, 7.0 Hz, 1H), 3.37 – 3.25 (m, 1H), 2.25 (t, *J* = 6.9, 1H), 1.68 (s, 3H), 1.06 – 0.86 (m, 18H), 0.80 (ddd, *J* = 8.6, 7.1, 0.9 Hz, 2H), 0.59 (q, *J* = 8.0 Hz, 9H), 0.15 (d, *J* = 7.5 Hz, 6H), -0.03 (s, 9H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 201.83, 170.06, 168.45, 166.95, 160.55, 158.27, 142.99, 136.96, 136.56, 131.14, 128.86, 128.68, 128.42, 126.74, 121.15, 117.29, 113.56, 109.06, 107.39, 91.09, 86.17, 71.84, 70.56, 69.83, 66.39, 66.02, 64.12, 35.14, 34.38, 26.06, 24.27, 18.52, 18.24, 7.11, 5.24, -1.26, -4.40, -4.61; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 1051.3986; found: 1051.3912 (ESI).



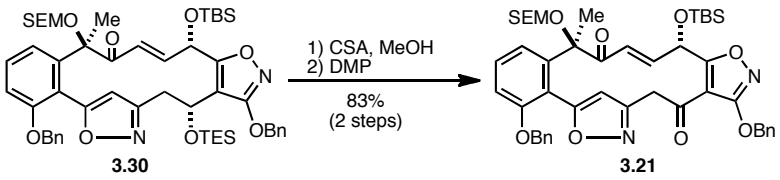

**3.29** **3.30**

**Macrocyclic-enone (3.30).** To a solution of **3.29** (430 mg, 0.410 mmol, 1.00 equiv.) in wet $CH_2Cl_2$ (4.1 mL, 0.10 M) at room temperature exposed to air, DMP (1.04 g, 2.46

mmol, 6.00 equiv.) was added in a single portion. The reaction was stirred for 1.5 h upon which time the cloudy mixture was poured into an Erlenmeyer flask containing pH 7 phosphate buffer (0.1 M buffer, 10 mL) and $Na_2S_2O_3$ (200 mg). The reaction flask was washed three times with 10 mL portions of hexanes and this was poured into the vigorously stirring mixture within the Erlenmeyer flask. After 20 minutes of vigorous mixing, the reaction was extracted three times with hexanes. The combined organic extracts were washed with brine, dried with $Na_2SO_4$, and concentrated *in vacuo* to yield crude aldehdye, which was immediately subjected to Reformatsky macrocyclization (*vide infra*).

A solution of intermediate aldehyde (0.410 mmol, crude from the reaction above) in degassed THF (21 mL, 0.020 M) at –78 °C under an atmosphere of argon was added to a solution of $SmI_2$ (25 mL of a 0.10 M solution in THF, 6.00 equiv.) at –78 °C via cannula directly into the solution over 10 minutes. THF (4.0 mL) was then used to wash the flask, and this too was added to the $SmI_2$ solution. The resulting dark blue solution was stirred at –78 °C for 25 minutes, upon which time air was bubbled through a glass pipet directly into the solution at –78 °C for 10 minutes until the blue color disappeared and a yellow color persisted. A solution of sat. $NaHCO_3$ (20 mL) also containing $Na_2S_2O_3$ (1 g) was added and the reaction was allowed to warm to room temperature. The mixture was then extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (5:1 hexanes:EtOAc) affording the intermediate macrocyclic alcohol (238 mg, 66%) as a mixture of secondary carbinol diastereomers that will be dehydrated in the next step.

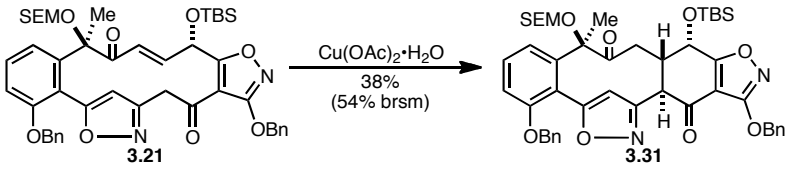
To the intermediate macrocyclic alcohol (238 mg, 0.245 mmol, 1.00 equiv.) in $CH_2Cl_2$ (4.9 mL, 0.050 M) at –78 °C under an atmosphere of nitrogen, the Martin sulfurane (4.9 mL of a 0.12 M solution in $CH_2Cl_2$, 2.5 equiv.) at room temperature was added along the side of the flask over 30 seconds. The reaction was allowed to warm to –20 °C over 25 minutes, and held at this temperature for 30 minutes. The reaction was quenched via the addition of sat. $NaHCO_3$ (5 mL), warmed to room temperature while stirring vigorously, and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (5:1 hexanes:EtOAc) affording **3.30** (203 mg, 87%) as a white foam. Yield for the three steps: 52%. $\boldsymbol{R_f}$ = 0.40 (3:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –50 (*c* 2.2, $CHCl_3$); **IR** (neat) 2954, 2878, 1701, 1628, 1577, 1511, 1458, 1273, 1250, 1079, 1009, 837, 744; **$^1$H NMR** (500 MHz, $d_6$-DMSO) δ 7.59 – 7.45 (m, 3H), 7.44 – 7.32 (m, 3H), 7.32 – 7.11 (m, 7H), 6.89 (s, 1H), 6.54 (s, 1H), 6.31 (s, 1H), 5.52 – 5.41 (m, 1H), 5.42 – 5.30 (m, 2H), 5.19 – 5.00 (m, 2H), 5.01 – 4.85 (m, 1H), 4.65 (dd, *J* = 61.4, 7.4 Hz, 2H), 3.71 – 3.58 (m, 1H), 3.53 – 3.36 (m, 2H), 3.00 (d, *J* = 12.7 Hz, 1H), 1.65 (s, 3H), 1.04 – 0.76 (m, 17H), 0.71 – 0.54 (m, 9H), 0.05 (d, *J* = 9.2 Hz, 6H), -0.02 (s, 9H); **$^{13}$C NMR** (126 MHz, $d_6$-DMSO) δ 200.04, 169.75, 166.43, 165.02, 157.65, 142.19, 136.69, 136.12, 130.86, 128.32, 128.28, 128.20, 128.06, 127.53, 127.47, 126.61, 126.46, 122.76, 120.48, 117.17, 113.65, 109.82, 106.49, 89.75, 83.83, 70.95, 69.37, 67.89, 64.83, 63.14, 32.73, 25.56, 25.44, 25.37, 22.69, 17.73, 17.50, 6.55, 6.51, 4.32, 4.23, -1.46, -1.48, -4.52, -5.14; **HRMS**: Exact mass calcd for [$(M+H^+)$]: 953.4618; found: 953.4622 (ESI).




**Elaborated macrocycle (3.21).** To a solution of **3.30** (490 mg, 0.514 mmol, 1.00 equiv.) in methanol (10 mL, 0.050 M) and $CH_2Cl_2$ (2.0 mL, 0.26 M) at 0 °C under an atmosphere of nitrogen, CSA (12 mg, 0.051 mmol, 0.10 equiv.) was added in a single portion. The resulting solution was stirred for 3 h, upon which time the reaction was quenched with sat. $NaHCO_3$ and warmed to room temperature. The resulting mixture was extracted three times with $CH_2Cl_2$, and the combined organic extracts were dried with $Na_2SO_4$, and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (4:1 hexanes:EtOAc) affording the intermediate alcohol (380 mg, 88%) as a colorless foam.

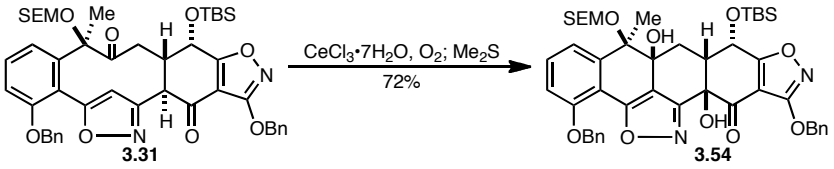
To a solution of the intermediate secondary carbinol (123 mg, 0.147 mmol, 1.00 equiv.) in wet $CH_2Cl_2$ (2.9 mL, 0.05 M) at room temperature exposed to air, DMP (374 mg, 0.882 mmol, 6.00 equiv.) was added in a single portion. The reaction was stirred for 1.5 h, upon which time the reaction was poured into an Erlenmeyer flask containing sat. $NaHCO_3$ (20 mL) and $Na_2S_2O_3$ (500 mg). The original reaction flask was washed liberally with hexanes and these washings were poured into the vigorously mixing solution. After 10 minutes, the mixture was poured into a sep. funnel, the organic layer was removed, and the remaining aqueous layer was extracted two times more with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (4:1 hexanes:EtOAc) affording **3.21** (116 mg, 94%) as a white foam. Yield for the two steps: 83%. $\boldsymbol{R_f}$ = 0.52 (3:1 hex-

anes:EtOAc); **IR** (neat) 2953, 2930, 1695, 1595, 1505, 1453, 1365, 1272, 1250, 1121, 1068, 1009, 838, 696; $[\alpha]_D$ = –129 (*c* 3.2, $CHCl_3$); **$^1$H NMR** (500 MHz, $d_6$-DMSO) δ 7.60 – 7.55 (m, 2H), 7.51 (t, *J* = 8.2 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.34 – 7.21 (m, 7H), 6.67 (d, *J* = 15.7 Hz, 1H), 6.42 – 6.04 (m, 2H), 5.84 (d, *J* = 8.1, 1H), 5.43 (dd, *J* = 11.9, 2H), 5.11 (dd, *J* = 12.9 Hz, 2H), 4.70 – 4.42 (m, 2H), 4.31 (d, *J* = 12.0 Hz, 1H), 3.83 (d, *J* = 12.1 Hz, 1H), 3.63 (td, *J* = 9.6, 7.3 Hz, 1H), 3.43 (td, *J* = 9.6, 7.2 Hz, 1H), 1.61 (s, 3H), 0.88 (s, 9H), 0.80 (ddd, *J* = 9.1, 6.8, 1.6 Hz, 2H), 0.08 (s, 6H), -0.00 (s, 9H); **$^{13}$C NMR** (126 MHz, $d_6$-DMSO) δ 199.31, 189.39, 174.99, 167.93, 166.40, 157.58, 155.46, 142.32, 141.33, 136.65, 135.30, 131.09, 128.51, 128.37, 128.29, 128.21, 128.10, 127.76, 127.62, 126.77, 122.83, 120.92, 116.33, 113.65, 107.84, 89.55, 83.99, 72.22, 69.52, 68.65, 64.95, 25.44, 22.33, 17.88, 17.51, -1.45, -4.98, -5.21; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 837.3597; found: 837.3566 (ESI).




**Transannular Michael product 3.31.** To **3.21** (55 mg, 0.066 mmol, 1.0 equiv.) in degassed methanol (3.3 mL, 0.02 M) at room temperature under an argon atmosphere, $Cu(OAc)_2$•$H_2O$ (66 mg, 0.33 mmol, 5.0 equiv.) was added in a single portion. The reaction was immediately sealed, and allowed to stir at room temperature for 22 h. The blue/green solution was quenched with sat. $NaHCO_3$ and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in*

*vacuo*. The crude residue was purified via flash chromatography on silica gel (5:1 hexanes:EtOAc → 4:1 hexanes:EtOAc → 3:1 hexanes:EtOAc) affording starting material **3.21** (16 mg, 29%) and Michael product **3.31**. The Michael product was further purified via HPLC (0.4% *i*-PrOH and hexanes) affording **3.21** (21 mg, 38%, 54% brsm) as a colorless oil. $\boldsymbol{R_f}$ = 0.52 (3:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = +9.7 (*c* 0.18, $CHCl_3$); **IR** (neat) 2882, 2852, 1709, 1624, 1574, 1511, 1472, 1362, 1262, 1118, 1000, 836, 780, 739, 696; **$^1$H NMR** (600 MHz, C6D6) δ 7.50 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.31 – 7.20 (m, 2H), 7.14 – 7.07 (m, 2H), 7.04 (ddt, *J* = 15.2, 8.2, 1.7 Hz, 4H), 6.99 – 6.93 (m, 1H), 6.52 (dd, *J* = 8.3, 0.8 Hz, 1H), 5.79 (s, 1H), 5.21 (m, 2H), 4.86 (d, *J* = 6.5 Hz, 1H), 4.73 (dd, *J* = 14.6, 6.2 Hz, 3H), 4.00 (d, *J* = 2.7 Hz, 1H), 3.88 (d, *J* = 10.2 Hz, 1H), 3.75 (td, *J* = 9.3, 7.1 Hz, 1H), 3.59 (td, *J* = 9.2, 7.0 Hz, 1H), 3.17 – 2.94 (m, 2H), 2.13 (d, *J* = 15.9 Hz, 1H), 1.74 (s, 3H), 0.92 (ddd, *J* = 9.3, 6.8, 2.4 Hz, 2H), 0.81 (s, 9H), 0.25 – -0.20 (m, 15H); **$^{13}$C NMR** (126 MHz, C6D6) δ 195.01, 184.09, 179.40, 170.55, 168.32, 158.91, 157.15, 150.15, 136.85, 135.73, 132.12, 128.88, 128.75, 128.58, 128.54, 127.13, 120.88, 116.47, 112.39, 111.74, 107.48, 92.44, 83.38, 72.43, 70.79, 66.61, 65.89, 49.84, 47.55, 42.24, 30.09, 25.83, 18.55, 18.32, -1.27, -1.33, -4.69, -5.01; **HRMS**: Exact mass calcd for [$(M+Na^+)$]: 859.3416; found: 859.3416 (ESI).



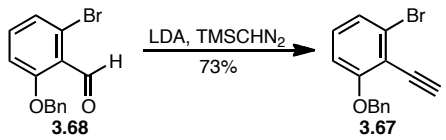

**Linear pentacycle 3.54.** To **3.31** (11 mg, 0.013 mmol, 1.0 equiv.) at room temperature in isopropanol (1.3 mL, 0.010 M), $O_2$ (from a balloon) was bubbled through the solution for 10 minutes. Next, $CeCl_3 \bullet 7H_2O$ (2.4 mg, 6.5 μmol, 0.50 equiv.) was added to the solution and the reaction was stirred vigorously while $O_2$ was continuously bubbled through the solution (a 21 gauge needle that was slightly blocked to reduce flow was used as an outlet). The reaction was stirred for 1 hour, during which time the solution became slightly yellow. Next, the reaction was immediately transferred to a silica gel column pre-equilibrated with EtOAc, and the reaction was passed through the column with 25 mL of EtOAc. The resulting solution was concentrated *in vacuo*.

The crude mixture was dissolved in $CH_2Cl_2$ (1.3 mL, 0.010 M) at room temperature under an atmosphere of nitrogen, and dimethyl sulfide (three drops) was added directly into the solution. The resulting clear solution was stirred at room temperature for 15 minutes, upon which time the reaction was concentrated directly *in vacuo*. The crude material was purified via column chromatography on silica gel (3:1 hexanes:EtOAc), affording **3.54** (8.0 mg, 72%) as a white solid. $\boldsymbol{R_f}$ = 0.07 (3:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = +52.6 (*c* 0.095, $CHCl_3$); **IR** (neat) 3379, 2956, 1708, 1655, 1613, 1573, 1512, 1476, 1371, 1260, 1023, 839, 687; **$^1$H NMR** (500 MHz, C6D6) δ 7.47 – 7.41 (m, 2H), 7.33 – 7.27 (m, 2H), 7.23 – 7.18 (m, 3H), 7.10 – 6.96 (m, 5H), 6.47 (d, *J* = 8.2 Hz, 1H), 5.84 (d, *J* = 5.8 Hz, 1H), 5.15 (m, 2H), 4.92 – 4.71 (m, 3H), 4.68 (d, *J* = 7.3 Hz, 1H), 4.38 (s, 1H), 3.83 (ddd, *J* = 12.5, 5.8, 2.0 Hz, 1H), 3.79 – 3.62 (m, 3H), 2.61 (dd, *J* = 13.7, 2.1 Hz, 1H),

1.87 (t, *J* = 13.2 Hz, 1H), 1.00 (s, 9H), 0.97 – 0.91 (m, 2H), 0.86 (s, 3H), 0.15 (d, *J* = 28.1 Hz, 6H), -0.04 (s, 9H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 184.38, 180.10, 163.77, 158.48, 155.22, 146.93, 137.15, 135.65, 131.68, 128.86, 128.68, 128.60, 128.58, 126.99, 119.53, 116.32, 114.03, 112.49, 104.38, 91.21, 86.07, 78.56, 72.52, 70.48, 70.37, 66.40, 64.77, 48.21, 29.52, 26.06, 23.51, 18.64, 18.32, -1.35; **HRMS**: Exact mass calcd for [(M-$H_2O$+$H^+$)]: 835.3441; found: 835.3391(ESI).


**Polycycle 3.55.** To a solution of **3.54** (8.0 mg, 0.0094 mmol, 1.0 equiv.) in THF (0.50 mL, 0.019M) at room temperature exposed to air, 4 *N* HCl (0.5 mL, 0.019 M) was added rapidly. The reaction was then sealed and stirred at room temperature for 24 h. The resulting slightly yellow solution was quenched with sat. $NaHCO_3$ (caution, gas evolution) and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (3:2 EtOAc:hexanes) affording **3.55** (4.7 mg, 85%) as a white solid. $R_f$ = 0.19 (1:1 hexanes:EtOAc); $[\alpha]_D$ = –240 (*c* 0.31, $CHCl_3$); **IR** (neat) 3426, 2925, 1715, 1668, 1619, 1572, 1514, 1453, 1288, 1027, 750; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.35 – 7.25 (m, 2H), 7.21 – 7.17 (m, 2H), 7.10 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.07 – 6.98 (m, 4H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.86 (t, *J* = 8.1 Hz, 1H), 6.44 (d, *J* = 8.3 Hz, 1H), 4.98 (d, *J* = 12.0 Hz, 1H), 4.80 (s, 1H), 4.76 – 4.66 (m, 2H), 4.60 (d, *J* = 12.5 Hz, 1H), 4.48 (d, *J* =

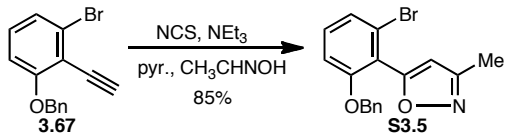
6.0 Hz, 1H), 2.74 (t, *J* = 5.5 Hz, 1H), 2.54 (d, *J* = 12.4 Hz, 1H), 2.06 (dd, *J* = 12.4, 5.0 Hz, 1H), 1.66 (s, 3H), 1.12 (s, 1H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 187.17, 176.80, 167.55, 161.86, 159.94, 155.19, 144.08, 136.80, 135.41, 131.62, 128.80, 128.66, 128.58, 128.54, 126.89, 119.46, 116.10, 113.62, 113.53, 105.80, 82.35, 74.73, 73.27, 72.51, 70.51, 69.40, 48.77, 33.98, 20.08; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 591.1762; found: 591.1754 (ESI).



**3.68** **3.67**

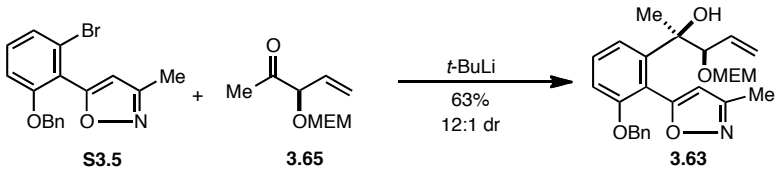
**1-(benzyloxy)-3-bromo-2-ethynylbenzene (3.67).** A flame-dried 3-necked 1 L flask equipped with a mechanical stirrer under an atmosphere of argon was charged with THF (320 mL, 0.30 M), followed by addition of diisopropylamine (16 mL, 0.114 mol, 1.20 equiv.) rapidly via syringe. This solution was cooled to 0 °C, and *n*-BuLi (38.2 mL of a 2.61 M solution in hexane, 0.100 mol, 1.05 equiv.) was added rapidly while keeping the internal temperature of the solution < 10 °C. After stirring for 25 minutes, the solution was cooled to –78 °C and $TMSCHN_2$ (50 mL of a 2.0 M solution in hexane, 0.100 mol, 1.05 equiv.) was added rapidly directly into the solution via syringe. The reaction was allowed to stir for 30 minutes at –78 °C, upon which time **3.68** (27.7 g, 95.0 mmol, 1.00 equiv.) in anhydrous THF (190 mL, 0.5 M) at –78 °C under nitrogen was added to the reaction mixture directly into the solution via cannula over 10 minutes. The resulting slightly orange solution was stirred for 10 minutes at –78 °C, upon which time it was warmed to room temperature by removal of the cooling bath. The reaction was stirred for

2.5 h, during which time the solution turned red/orange and slow bubbling was observed. The resulting clear orange solution was quenched with sat. $NH_4Cl$ and stirred for 2 h, upon which time the mixture was extracted three times with hexanes. The combined organic extracts were washed once with brine, dried with $Na_2SO_4$, and concentrated *in vacuo*. The crude residue was purified via trituration with hexanes affording **3.67** (20.0 g, 73%) as a white powder that was homogeneous by NMR and TLC. $\boldsymbol{R_f}$ = 0.62 (5:1 hexanes:EtOAc); **MP** = 54 – 56 °C; **IR** (neat) 3288, 1583, 1562, 1438, 1380, 1269, 1024, 871; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.10 (t, *J* = 8.2 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 5.19 (s, 2H), 3.63 (s, 1H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 161.22, 136.46, 130.26, 128.74, 128.10, 127.16, 126.98, 125.03, 114.81, 111.43, 86.41, 78.53, 70.90; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 287.0066; found: 287.0072 (ESI).



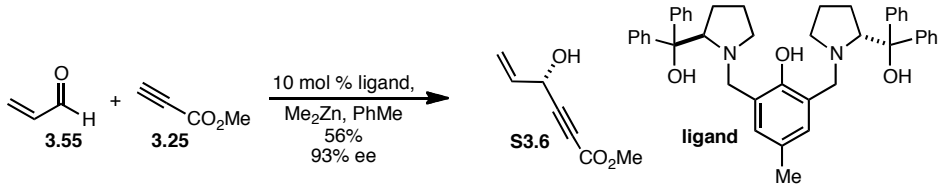

**5-(2-(benzyloxy)-6-bromophenyl)-3-methylisoxazole (S3.5).** To a solution of acetaldoxime (0.424 mL, 6.96 mmol, 4.00 equiv.) in $CH_2Cl_2$ (8.5 mL, 0.82 M) at room temperature under an atmosphere of nitrogen, pyridine (0.014 mL, 0.17 mmol, 0.10 equiv.) was added. To this solution, NCS (929 mg, 6.96 mmol, 4.00 equiv.) was added in a single portion, and the resulting mixture was stirred for 5 minutes. This solution was then drawn into a gas-tight syringe and added to a mixture of **3.67** (500 mg, 1.74 mmol, 1.00 equiv.) in chloroform (17 mL, 0.10 M) at 60 °C over 24 h via a Teflon® tube connecting the syringe

to the flask. The reaction was poured into a separatory funnel containing water, and extracted three times with $CH_2Cl_2$. The combined organic extracts were washed once with brine, dried with $Na_2SO_4$, and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (6:1 hexanes:EtOAc → 5:1 hexanes:EtOAc) affording **S3.5** (508 mg, 85%) as a slightly yellow solid. $R_f$ = 0.56 (5:1 hexanes:EtOAc); **IR** (neat) 3065, 3033, 2930, 1622, 1567, 1444, 1410, 1273, 1241, 1023; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 2H), 7.32 – 7.26 (m, 3H), 7.23 (t, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.26 (s, 1H), 5.10 (s, 2H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 165.77, 159.59, 158.12, 136.22, 132.07, 128.69, 128.06, 126.87, 125.62, 124.71, 119.96, 112.08, 106.49, 70.88, 11.77; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 344.0281; found: 344.0290 (ESI).



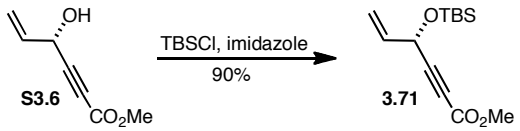

**(2*R*,3*R*)-2-(3-(benzyloxy)-2-(3-methylisoxazol-5-yl)phenyl)-3-((2-methoxyethoxy) meth-oxy)pent-4-en-2-ol (3.63).** To **S3.5** (425 mg, 1.23 mmol, 1.00 equiv.) co-evaporated once with benzene, $Et_2O$ (12 mL, 0.10 M) was added, and the solution was cooled to –78 °C under an atmosphere of argon. Next, *t*-BuLi (1.41 mL of a 1.79 M solution in pentane, 2.52 mmol, 2.05 equiv.) was added dropwise over 60 seconds. The cloudy solution was then stirred for an addition 60 seconds. To this solution, **3.65** (255 mg, 1.35 mmol, 1.10 equiv.) in THF (12 mL, 0.11 M) at room temperature was added over 3 minutes directly into the solution via syringe. The resulting clear yellow solution

was stirred at –78 °C for 25 minutes, upon which time it was quenched with sat. $NH_4Cl$ and warmed to room temperature. The resulting mixture was diluted with water and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via MPLC (10% → 60% EtOAc and hexanes) affording **3.63** (350 mg, 63%) as a white foam. $R_f$ = 0.36 (1:1 hexanes:EtOAc); $[\alpha]_D$ = –37 (*c* 0.70, $CHCl_3$); **IR** (neat) 3448, 2981, 2933, 2887, 1612, 1572, 1452, 1413, 1265, 1106, 1027; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.1 Hz, 2H), 7.32 (dd, *J* = 8.0, 6.4 Hz, 2H), 7.28 (t, *J* = 3.6 Hz, 1H), 7.26 – 7.19 (m, 3H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.23 (s, 1H), 5.84 – 5.70 (m, 1H), 5.34 (dd, *J* = 10.3, 1.8 Hz, 1H), 5.22 (dd, *J* = 17.4, 1.7 Hz, 1H), 5.04 (s, 2H), 4.69 (d, *J* = 7.0 Hz, 1H), 4.52 (d, *J* = 7.0 Hz, 1H), 4.39 (d, *J* = 8.2 Hz, 1H), 3.30 (s, 3H), 3.29 – 3.16 (m, 2H), 3.07 – 2.95 (m, 1H), 2.38 (s, 3H), 1.34 (s, 3H); **$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 167.84, 159.47, 157.80, 148.51, 136.84, 133.38, 130.65, 128.55, 127.81, 126.67, 121.16, 120.00, 116.67, 111.35, 106.50, 92.57, 83.48, 77.25, 71.62, 70.59, 67.05, 59.03, 26.12, 11.75; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 454.2224; found: 454.2230 (ESI).



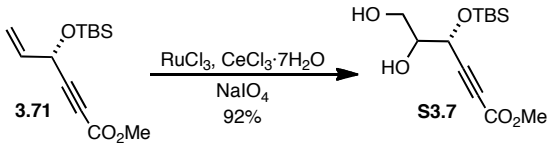

**(*R*)-methyl 4-hydroxyhex-5-en-2-ynoate (S3.6).** To a solution of *R*-*R*-bis-prophenol **ligand** (2.00 g, 3.13 mmol, 0.100 equiv.) in toluene (160 mL, 0.20 M wrt aldehyde **3.55**) at room temperature under an atmosphere of nitrogen, methyl propiolate **3.25** (8.35 mL,

93.9 mmol, 3.00 equiv.) was added rapidly via syringe followed by acrolein (2.09 mL, 31.3 mmol, 1.00 equiv.). Next, dimethylzinc (78 mL of a 1.2 M solution in toluene, 93.9 mmol, 3.00 equiv.) was added rapidly via syringe to the solution (caution, gas evolution). The resulting slightly yellow solution was stirred for ten minutes with an outlet needle allowing the gas to escape. Next, the reaction was sealed, transferred to a 4 °C bath and stirred for 48 h. The reaction was then cooled to 0 °C, carefully quenched via addition of sat. $NH_4Cl$ (caution, gas evolution) and extracted three times with $Et_2O$. The combined organic extracts were washed once with brine, dried with $Na_2SO_4$ and concentrate *in vacuo*. The crude material was purified via flash chromatography on silica gel (hexanes → 8:1 hexanes:EtoAc → 4:1 hexanes:EtOAc) affording **S3.6** (2.45 g, 56% yield, 93% ee) as a slightly yellow liquid. $\boldsymbol{R_f}$ = 0.42 (4:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = +33 (*c* 0.75, $CHCl_3$); **IR** (neat) 3404, 2344, 2239, 1719, 1437, 1254, 1124, 1027, 987, 952, 892; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 5.97 (ddd, *J* = 17.1, 10.2, 5.3 Hz, 1H), 5.52 (dd, *J* = 17.0, 1.6 Hz, 1H), 5.40 – 5.27 (m, 1H), 5.01 (ddd, *J* = 8.5, 4.2, 1.5 Hz, 1H), 3.80 (s, 3H), 1.98 (d, *J* = 6.9 Hz, 1H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 153.80, 134.90, 118.15, 85.70, 77.51, 62.94, 53.04. **HRMS** could not obtain mass via ESI.



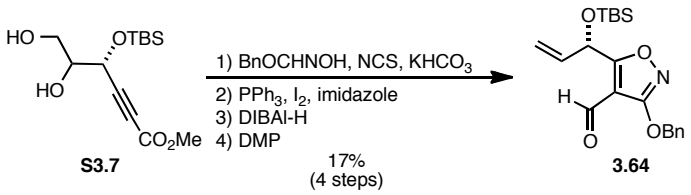

**(*R*)-methyl 4-((*tert*-butyldimethylsilyl)oxy)hex-5-en-2-ynoate (3.71).** To a solution of **S3.6** (2.58 g, 18.1 mmol, 1.00 equiv.) in DMF (37 mL, 0.50 M) at 0 °C under an atmosphere of nitrogen, imidazole (1.97 g, 29.0 mmol, 1.6 equiv.) was added in a single portion,

followed TBSCl (3.55 g, 23.5 mmol, 1.30 equiv.) also in a single portion. The reaction was stirred for 3 h, upon which time it was quenched with sat. $NaHCO_3$ and extracted three times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography (20:1 hexanes:EtOAc) affording **3.71** (4.15 g, 90%) as a colorless oil. $\boldsymbol{R_f}$ = 0.69 (4:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –57 (*c* 1.45, $CHCl_3$); **IR** (neat) 2956, 2931, 2859, 2239, 1721, 1436, 1253, 1082, 1033, 839; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 5.89 (ddd, *J* = 17.0, 10.1, 5.0 Hz, 1H), 5.44 (dt, *J* = 16.9, 1.3 Hz, 1H), 5.22 (dt, *J* = 10.1, 1.3 Hz, 1H), 5.00 (dt, *J* = 5.0, 1.6 Hz, 1H), 3.78 (s, 3H), 0.92 (s, 9H), 0.15 (d, *J* = 10.9 Hz, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 153.77, 135.80, 116.33, 86.55, 76.65, 63.43, 52.72, 25.74, 18.29, -4.61, -4.91; **HRMS**: Exact mass calcd for [$(M+Na^+)$]: 277.1230; found: 277.1225 (ESI).




**(4*S*)-methyl 4-((*tert*-butyldimethylsilyl)oxy)-5,6-dihydroxyhex-2-ynoate (S3.7).** To a 100 mL flask, $NaIO_4$ (4.90 g, 22.8 mmol, 1.50 equiv.) was added, followed by water (7.6 mL, 2.0 M) and $CeCl_3$•$7H_2O$ (566 mg, 0.387 mmol, 10 mol %). A heat gun was used to heat the cloudy suspension until it became a persistent yellow mixture (approximately 30 seconds). This suspension was cooled to 0 °C, and acetonitrile (23 mL, 0.66 M) and EtOAc (19 mL, 0.80 M) were added sequentially. Next, $RuCl_3$ (16 mg, 0.076 mmol, 0.5 mol %) in water (1.0 mL) was added rapidly. After 60 seconds of stirring, **3.71** (3.87 g, 15.2 mmol, 1.00 equiv.) in EtOAc (8.0 mL, 1.9 M) was added via syringe. The reaction

was stirred vigorously while open to air at 0 °C for 15 minutes, after which time the reaction was filtered through a plug of cotton. The filtrate was diluted with brine, and shaken in a separatory funnel. The resulting aqueous layer (yellow) was removed, and the remaining organic layer was washed with sat. $Na_2S_2O_3$, dried with $Na_2SO_4$, and concentrated *in vacuo*. The crude residue was purified via flash chromatography (1:1 hexanes:EtOAc) affording the white foam **S3.7** (4.03 g, 92%) as a 1.6:1 ratio of diastereomers. The diastereomers could be further separated via HPLC (2.5% *i*-PrOH and hexanes). The major diastereomer could be completely separated and was therefore the compound that was characterized: $\mathbf{R_f}$ = 0.64 (1:1 hexanes:EtOAc); $\mathbf{[\alpha]_D}$ = –60 (*c* 0.65, $CHCl_3$); **IR** (neat) 3418, 2956, 2931, 2859, 2240, 1721, 1472, 1436, 1254, 1105, 1061, 840; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 4.61 (d, *J* = 4.7 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.84 – 3.72 (m, 4H), 2.68 (d, *J* = 6.6 Hz, 1H), 2.05 (s, 1H), 0.92 (s, 9H), 0.18 (d, *J* = 18.0 Hz, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 153.64, 85.74, 77.92, 73.65, 65.53, 62.86, 53.02, 25.77, 18.21, -4.57, -5.15; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 311.1285; found: 311.1289 (ESI).




**(*S*)-3-(benzyloxy)-5-(1-((*tert*-butyldimethylsilyl)oxy)allyl)isoxazole-4-carbaldehyde (3.64).** To a solution of **S3.7** (500 mg, 1.73 mmol, 1.00 equiv.) in EtOAc (17 mL, 0.10 M) at room temperature exposed to air, BnOCHNOH (131 mg, 0.865 mmol, 0.500

equiv.) was added, followed by the addition of $KHCO_3$ (1.73 g, 17.3 mmol, 10.0 equiv.) and NCS (116 mg, 0.865 mmol, 1.00 equiv.). The flask was fitted with a reflux condensor, and the suspension was heated to 48 °C under an atmosphere of nitrogen for 12 h. The reaction was treated with an additional 0.500 equiv. of oxime and NCS every 12 h for a total 10 additions or 5 equiv. of each. The resulting cloudy and slightly yellow mixture was poured into a separatory funnel containing water and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. This crude material was purified via MPLC (10% → 50% EtOAc and hexanes) affording the intermediate isoxazole (350 mg, 46%) as a mixture of secondary carbinol diastereomers.

The intermediate isoxazole (680 mg, 1.55 mmol, 1.00 equiv.) in THF (15.5 mL, 0.10 M) at room temperature exposed to air was treated with $PPh_3$ (1.22 g, 4.65 mmol, 3.00 equiv.). Next, imidazole (633 mg, 9.30 mmol, 6.00 equiv.) was added, followed by $I_2$ (1.18 g, 4.65 mmol, 3.00 equiv.). The reaction was sealed and heated to 50 °C for 3 h upon which time the brown solution was poured into a separatory funnel containing sat. $NaHSO_3$ and the mixture was extracted three times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The resulting crude material was purified via flash chromatography on silica gel (20:1 hexanes : EtOAc) affording the intermediate ester (310 mg, 50%) as a colorless oil.

The intermediate ester (310 mg, 0.768 mmol, 1.00 equiv.) was dissolved in toluene (10 mL, 0.08 M) and cooled to –78 °C under an atmosphere of nitrogen. Next, DIBAl-H (2.3 mL of a 1.0 M solution in toluene, 2.30 mmol, 3.00 equiv.) was added along the side

of the flask over 10 seconds. The reaction was then stirred at –78 °C for 50 minutes, upon which time a 20 wt% solution of Rochelle's salt (10 mL) was added. The reaction was then allowed to warm to room temperature, upon which time it was poured into an Erlenmeyer flask containing water and EtOAc, and stirred vigorously for 30 minutes. The resulting solution was extracted three times with EtOAc. The combined organic extracts were washed once with brine, dried with $Na_2SO_4$, and concentrated *in vacuo*. The resulting crude residue was purified via flash chromatography on silica gel (5:1 hexanes:EtOAc) affording intermediate primary alcohol (248 mg, 76%) as a colorless liquid.

The intermediate primary alcohol (35 mg, 0.093 mmol, 1.00 equiv.) in wet $CH_2Cl_2$ (3.1 mL, 0.03 M) at room temperature exposed to air was treated with DMP (47 mg, 0.11 mmol, 1.2 equiv.) and the reaction was stirred for 1 hour. The reaction was quenched via addition of a sat. $NaHCO_3$ and $Na_2S_2O_3$, diluted with hexanes, and stirred vigorously until the mixture became clear (10 minutes). The resulting biphasic mixture was poured into a separatory funnel, the hexanes layer removed, and the remaining aqueous layer was extracted twice more with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. Aldehyde **3.64** was used without any further purification (35 mg, quant.). Yield for the 4 steps: 17%. $\mathbf{R_f}$ = 0.75 (6:1 hexanes:EtOAc); $\mathbf{[\alpha]_D}$ = –52 (*c* 0.75, $CHCl_3$); **IR** (neat) 2955, 2930, 2858, 1693, 1605, 1508, 1463, 1363, 1255, 1066, 939, 839; $^{1}$**H NMR** (500 MHz, $C_6D_6$) δ 9.76 (s, 1H), 7.20 – 7.16 (m, 2H), 7.10 – 6.98 (m, 3H), 5.89 (ddd, *J* = 16.8, 10.1, 6.0 Hz, 1H), 5.84 – 5.80 (m, 1H), 5.41 (dt, *J* = 16.8, 1.3 Hz, 1H), 5.06 (d, *J* = 1.1 Hz, 2H), 4.96 (dt, *J* = 10.0, 1.3 Hz, 1H), 0.89 (s, 9H), -0.01 (d, *J* = 8.3 Hz, 6H); $^{13}$**C NMR** (126 MHz, $C_6D_6$) δ 182.53, 178.15, 169.88, 135.78, 135.61,

128.75, 128.61, 128.35, 117.34, 107.49, 72.32, 69.63, 25.82, 18.39, -4.92, -5.05; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 396.1602; found: 396.1604 (ESI).

**B. Computational Methods**

*Molecular Mechanics*. All molecular mechanics calculations were performed using Spartan 2008, v. 1.1.2 (Wavefunction, Inc., Irvine, CA, USA), using the molecular mechanics MM2 force field. To generate an initial subset of reasonable conformers, a conformer distribution calculation was performed, and the 100 structures of lowest energy were documented. This procedure was performed at least three times with three different starting conformers, generating a total of 300 conformers for each macrocyclic enolate. A subset of these conformers was then further optimized via DFT.

*Density Functional Theory.* All DFT calculations were performed using Gaussian 09 (Revision A.02)[144] on the Odyssey Cluster at Harvard University. Each starting structure, already a local minimum with respect to the MM PES, was re-optimized with the B3LYP hybrid functional[145] with the 6-31G* (for H, C, O, and N) and MDF10 (for Cu) basis sets. Both restricted and unrestricted B3LYP calculations were performed with macrocycle **2.3**, however no major discrepancies were observed between the energy values. For

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[144] Gaussian 09, Revision A.02: Frisch, M. J.; Trucks. G. W.; Schlegel, H. B.; Scuseria G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann. R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian Inc., Wallingford, CT, **2009**.

this reason, RB3LYP was used preferentially. The SMD implicit solvation model[146] was used in all cases with methanol as the specified solvent.

*Enolate Chlorination.* Enolate chlorination utilized the optimized enolate and chlorine geometries listed in Appendix 4. Starting with a C12a-$Cl_2$ distance of 3.5 Å on either side of the enolate, the distance was iteratively contracted at a pace of 0.1 Å until a C12a-$Cl_2$ distance of 2.1 Å was achieved. During this scan, the Cl-Cl bond distance increased as is expected during a bond-forming/bond-breaking event. Scans were conducted using B3LYP/6-31g(d). All energy values are reported as electronic energy [E(RB+HF-LYP)].

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[145] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Chem. Phys.* **1994**, *98*, 11623-11627.

[146] Marenich, A. V.; Cramer. C. J.; Truhlar, D. G. *J. Phys. Chem. B.* **2009**, *113*, 6378-6396.

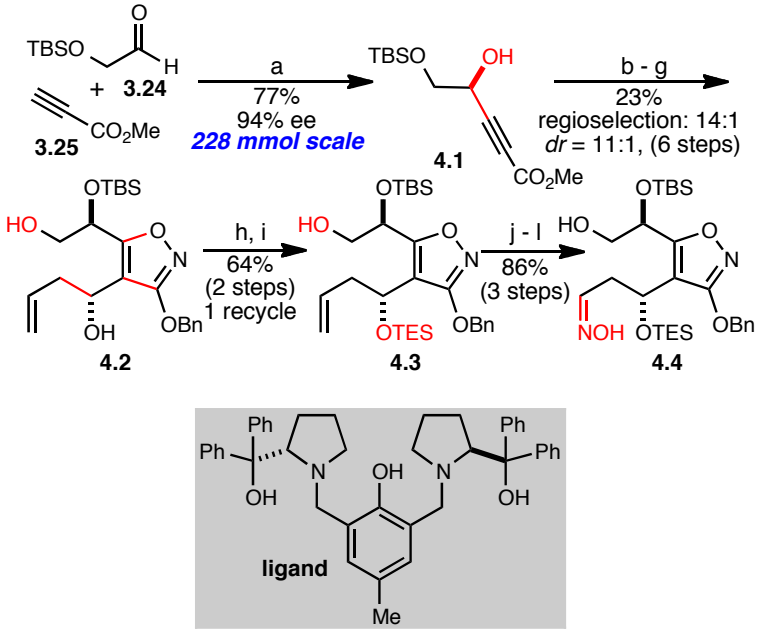
# *Chapter 4*

## Execution of a Transannular Cascade

### I. Synthesis of a New Macrocyclic Diastereomer

With the synthesis plan now modified to incorporate a new macrocyclic diastereomer, we embarked upon the construction of the requisite eastern fragment **4.4** (Scheme 4.1). Simply switching enantiomers of the bis-prophenol ligand used in the initial asymmetric zinc acetylide addition allowed us to synthesize **4.1** in an analogous manner to that discussed in Scheme 3.5. Notably, this reaction was scaled to 228 mmol of starting aldehyde in a single batch without a decrease in ee or yield. Subsequent elaboration to **4.4** was performed in a similarly analogous manner to the previous fragment. However, the protecting group manipulation required to convert **4.2** to **4.3** was improved significantly via the implementation of improved conditions for selective silyl deprotection. Under optimized conditions employing a THF/AcOH/$H_2O$ solvent system, the efficiency of primary TES deprotection was improved to a yield of 76% with one recycle. Subsequent elaboration to oxime **4.4** was uneventful.

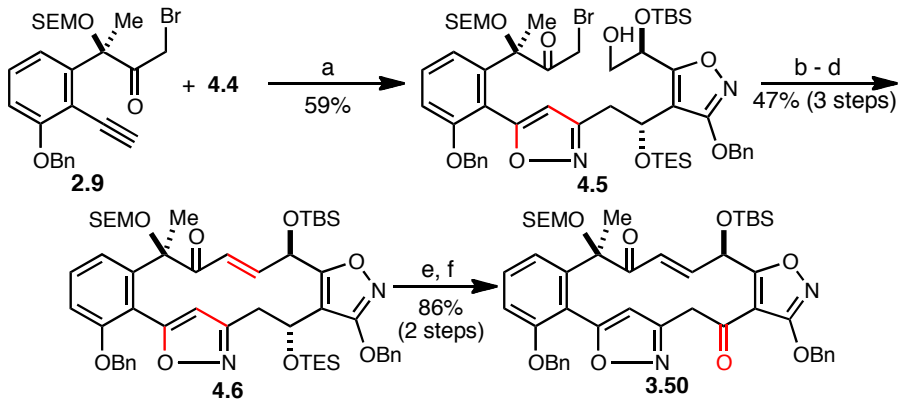
**Scheme 4.1** Synthesis of oxime **4.4**.




Reagents and conditions: (a) $Me_2Zn$, 9 mol % **ligand**, PhMe, –10 °C; 77%, 94% ee; (b) TBSCl, imidazole, DMF, 0 °C; (c) NCS, $KHCO_3$, BnOCHNOH, EtOAc, 48 °C; (d) DIBAl-H, toluene, –78 °C; (e) $SO_3$•pyr., DIPEA, $CH_2Cl_2$, DMSO, 0 °C; (f) (+)-$IPC_2Ballyl$, $Et_2O$, pentane, –110 °C → –78 °C; (g) HF•pyr., pyr., THF, rt; 23% (6 steps), 14:1 regioselection, *dr* = 11:1; (h) TESCl, imidazole, DMF, 0 °C; 84%; (i) AcOH, $H_2O$, THF, rt; 76% (1 recycle); (j) $OsO_4$, NMO, THF, acetone, pH 7 buffer, rt; $NaIO_4$, THF, pH 7 buffer, rt; $H_2NOH$•HCl, pyr., EtOH, 0 °C; 86% (3 steps).

Fragment coupling of **2.9** and **4.4** proceeded in good yield to produce bromoketone **4.5** (Scheme 4.2). This compound was immediately subjected to a two-step oxidation/Reformatsky sequence producing **4.6** after dehydration. Lastly, the remaining TES silyl ether was cleaved under acidic conditions, and the resulting alcohol was oxidized to produce elaborated macrocycle **3.50**. For completeness, a spectral comparison of macrocycles **2.3**, **3.21**, and **3.50** can be found in Figure 4.1.

**Scheme 4.2** Fragment coupling and elaboration to macrocycle **3.50**.




Reagents and conditions: (a) 1.20 equiv. **2.9**, 1.00 equiv. **4.4**, NCS, pyr.; DIPEA, $CHCl_3$, 40 °C to 50 °C; 59%; (b) DMP, $CH_2Cl_2$, rt; (c) $SmI_2$, THF, –78 °C; (d) Martin sulfurane, $CH_2Cl_2$, –78 °C to –20 °C; 69% (2 steps); (e) CSA, MeOH, $CH_2Cl_2$, 0 °C; (f) DMP, $CH_2Cl_2$, rt; 62% (3 steps).

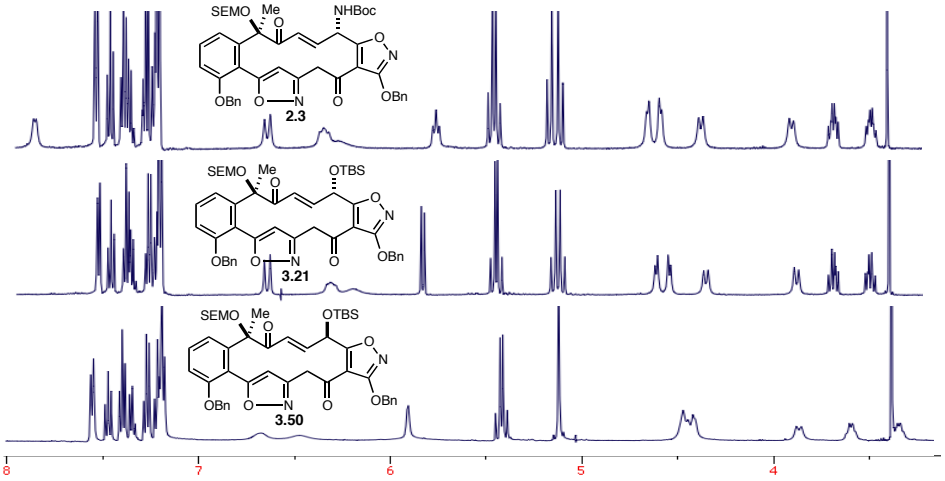
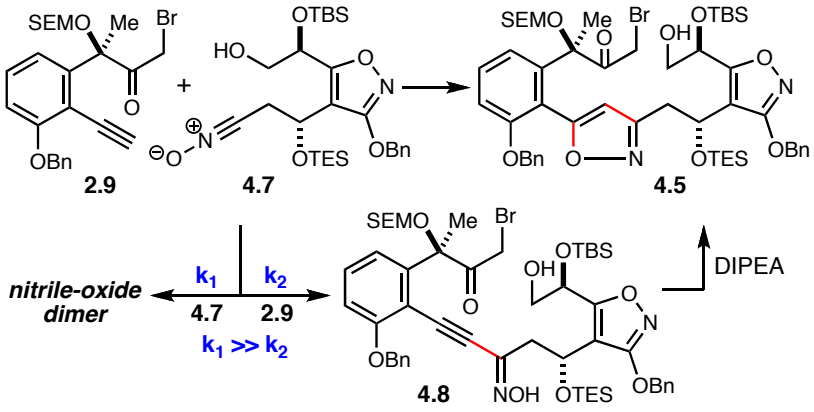



**Figure 4.1** $^1$H NMR spectral comparison of macrocycle **2.3** (upper), **3.21** (middle), and **3.50** (lower) in $d_6$-DMSO.

The intermolecular [3+2] cycloaddition that was used to couple fragments **2.9** and **4.4** deserves special mention, as this reaction is an improved procedure to that of the coupling of fragments **2.9** and **3.23** in the previous route. Upon study of the reaction, it be-

came apparent that the cycloaddition occurs via a stepwise process in our system.[147] Specifically, nitrile-oxide **4.7** is coupled with alkyne **2.9** to yield an isolable oxime intermediate (**4.8**, Scheme 4.3). However, this coupling process is slow compared to the rate of nitrile-oxide dimerization, which is a known decomposition pathway.[148] In order to keep the concentration of nitrile-oxide low enough such that the coupling of **2.9** and **4.7** could outcompete dimerization, we realized that heating the reaction to 40 °C while slowly generating **4.7** via syringe-pump addition of DIPEA was necessary. Extended heating of **4.8** in the presence of DIPEA then completed the cyclization process.[149]

**Scheme 4.3** Mechanistic proposal for the intramolecular [3+2] cycloaddition used to couple fragments **2.9** and **4.7**.




## II. Macrocyclic Stereocontrol

With the synthesis of macrocycle **3.50** complete, the transannular Michael reaction was executed using the established conditions. This macrocycle furnished the desired C4a-

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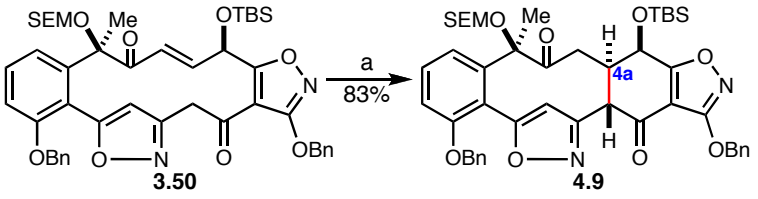
[147] This observation has been reported previously: Morrocchi, S.; Ricca, A.; Zanarotti, A. *Tet. Lett.* **1969**, *39*, 3329-3332.

[148] (a) Bode, J. W.; Carreira, E. M. *J. Org. Chem.* **2001**, *66*, 6410-6420. (b) Brinkmann, Y.; Madhushaw, R. J.; Jazzar, R.; Bernardinelli, G.; Kündig, E. P. *Tetrahdron* **2007**, *63*, 8413-8419. (c) Grecian, S.; Fokin, V. V. *Angew. Chem.* **2008**, *120*, 8409-8411.

[149] This conversion was monitored via TLC.

diastereomer **4.9** in excellent yield and as a sole detectable isomer (Scheme 4.4).[150,151] The successful execution of this reaction not only validated our stereochemical hypothesis that was developed as a result of our computational and experimental data (*vide supra*), but more importantly it allowed us to proceed with the remainder of our synthesis plan toward tetracycline.

**Scheme 4.4** Transannular Michael addition.




Reagents and conditions: (a) $Cu(OAc)_2 \cdot H_2O$, MeOH, rt; 83%.

With the first of two important stereochemical relationships now validated (C4-C4a), we decided to test whether the C4-C12a relationship would allow hydroxylation to proceed as planned. While the outright hydroxylation of Michael product **4.9** would have been completely reasonable at this juncture, we were captivated by the fact that it may be possible to produce the tetracycline core in a single reaction via a one-pot cascade (Scheme 4.5). Thus, we considered a variation of the cascade reported in Chapter 2, with the exception being the use of an alternative cerium source (other than $CeCl_3 \cdot 7H_2O$) such that C12a-chlorination is avoided.

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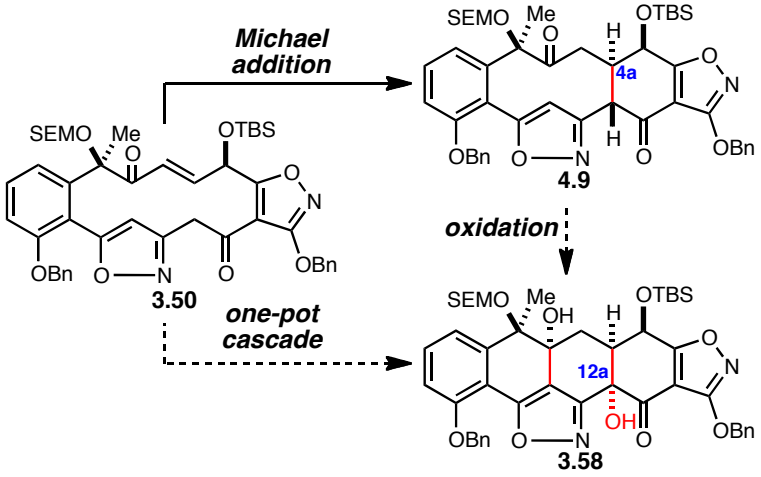
[150] The improved yield is most likely due to the decreased reaction time necessary for complete conversion (approximately 2 h vs. > 24 h).

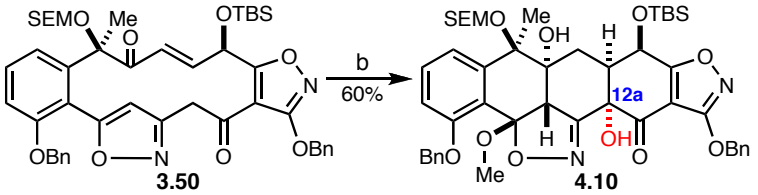
[151] The stereochemical assignment was based upon nOe and coupling constant data. Please see the supporting information for details.

**Scheme 4.5** Possible pathways towards the synthesis of **3.58** involve a two-step procedure or a potential reaction cascade.




Employing optimized conditions aimed at the execution of a transannular cascade, we subjected macrocycle **3.50** to both $Cu(OAc)_2 \cdot H_2O$ and $Ce(OAc)_3 \cdot (H_2O)_n$ in methanol as solvent. In the marquee reaction of the synthesis, we were able to effect the formation of **4.10**, which represents the product of a cascade to produce two transannular bonds and 5 stereogenic centers as a sole detectable diasteromer.[152] Further, we were able to reduce the loading of $Cu(OAc)_2 \cdot H_2O$ to 5 mol %, demonstrating the facile nature of the Michael addition. It was at this juncture that we experimentally established the solution to stereochemical interplay at C4, C4a, and C12a.

**Scheme 4.6** A successful reaction cascade.




Reagents and conditions: 5 mol % $Cu(OAc)_2 \cdot H_2O$, 4 equiv. $Ce(OAc)_3 \cdot (H_2O)_n$, $O_2$, MeOH, rt; 60%.

[152] A small amount of the des-methanol adduct was also obtained; however this was inconsequential since in a subsequent step the methanol is intentionally removed via treatment with acid.

### III. Proposed Mechanism of the Michael Reaction

The success of the Michael reaction to produce **4.9** can be attributed to both an understanding of the conformational profile of macrocycle **3.50** and the unique aptitude for $Cu(OAc)_2 \bullet H_2O$ to mediate the reaction. While we had thoroughly studied the former, we still did not understand the mechanism of the Michael reaction to a satisfactory degree. While Michael reactions employing copper enolates have been studied in related systems,[153,154] we were intrigued by several unique features of the Michael reaction at hand. First, the Michael reaction required methanol as solvent. This is in contrast to literature precedent, which reports the use of benzene,[153b,c] dichloromethane or toluene.[153d] Second, exceptionally high selectivity for a *trans* ring fusion was observed in all of the Michael reactions conducted, regardless of the stereochemical outcome.

With these two interesting features in mind, we looked to assemble a more transparent mechanistic picture by extrapolating our previous computational results into a transition state study. To minimize computational cost, we chose to use the first generation macrocycle containing a C4-NHBoc substituent, **2.3** (Scheme 4.7).[155] Further, both the SEM and benzyl protecting groups were truncated for this analysis. Since the conformational profile of this macrocycle has already been computed (*vide supra*), the low energy conformer was used as the starting point for the transition state study.

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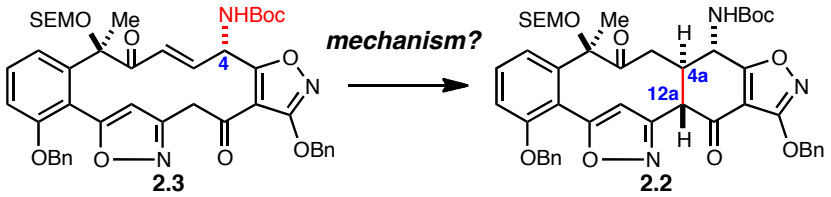
[153] (a) Saegusa, T.; Ito, Y.; Tomita, S.; Kinoshita, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 496-499. (b) Howells, P. N.; Kenney, J. W.; Nelson, J. H.; Henry, R. A. *Inorg. Chem.* **1976**, *15*, 124-129. (c) Eckberg, R. P.; Henry, R. A.; Cary, L. W.; Nelson, J. H. *Inorg. Chem.* **1977**, *16*, 2977-2979. (d) Pérez, E.; Moreno-Mañas, M.; Sebastián, R. M.; Vallribera, A.; Jutand, A. *Eur. J. Inorg. Chem.* **2010**, 1013-1019.

[154] For examples of lithium enolates participating in Michael reactions, see: (a) Heathcock, C. H.; Henderson, M. A. *J. Org. Chem.* **1985**, *50*, 3019-3022. (b) Oare, D. A.; Heathcock, C. H. *J. Org. Chem.* **1990**, *55*, 157-172. (c) Kwan, E. E.; Evans, D. A. *Org. Lett.* **2010**, *12*, 5124-5127.

[155] This decision was due to the increased computational cost associated with silyl-based protecting groups.

**Scheme 4.7** Transformation to be studied computationally.




The beginning of our proposed catalytic cycle involves the *in situ* formation of a copper(II) species competent for catalysis (Scheme 4.8). The reagent required to facilitate the Michael reaction, $Cu(OAc)_2 \bullet H_2O$, exists as a dimeric species with a characteristic "paddle-wheel" configuration of four bridging acetate ligands, two apical water ligands, and a metal-metal bond.[156] Exchange of the water ligands with methanol from solvent produces **4.11**, which may be driven to the monomer **4.12** in protic media.[157]

Copper complex **4.12** is proposed to undergo reversible dissociation of a methanol ligand with subsequent complexation of macrocycle **3.50**. This is immediately followed by an acetate-mediated deprotonation of the macrocycle to form **4.13**. Enolate **4.13**, which was originally studied in the context of our ground-state conformational analysis of macrocyclic enolates, is considered the most likely structure to proceed through the major transition state.[158] Not only is the structure readily formed following enolization (implying that it is "on-cycle"), but the bridging methanol ligand confers stabilization by acting as a hydrogen bond donor to the forming enolate as the Michael reaction proceeds.

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[156] van Niekerk, J. N.; Schoening, F. R. L. *Nature* **1953**, *171*, 36-37.

[157] Sharrock, P.; Melník, M. *Can. J. Chem.* **1985**, *63*, 52-56.

**Scheme 4.8** Proposed mechanism for the Michael reaction.

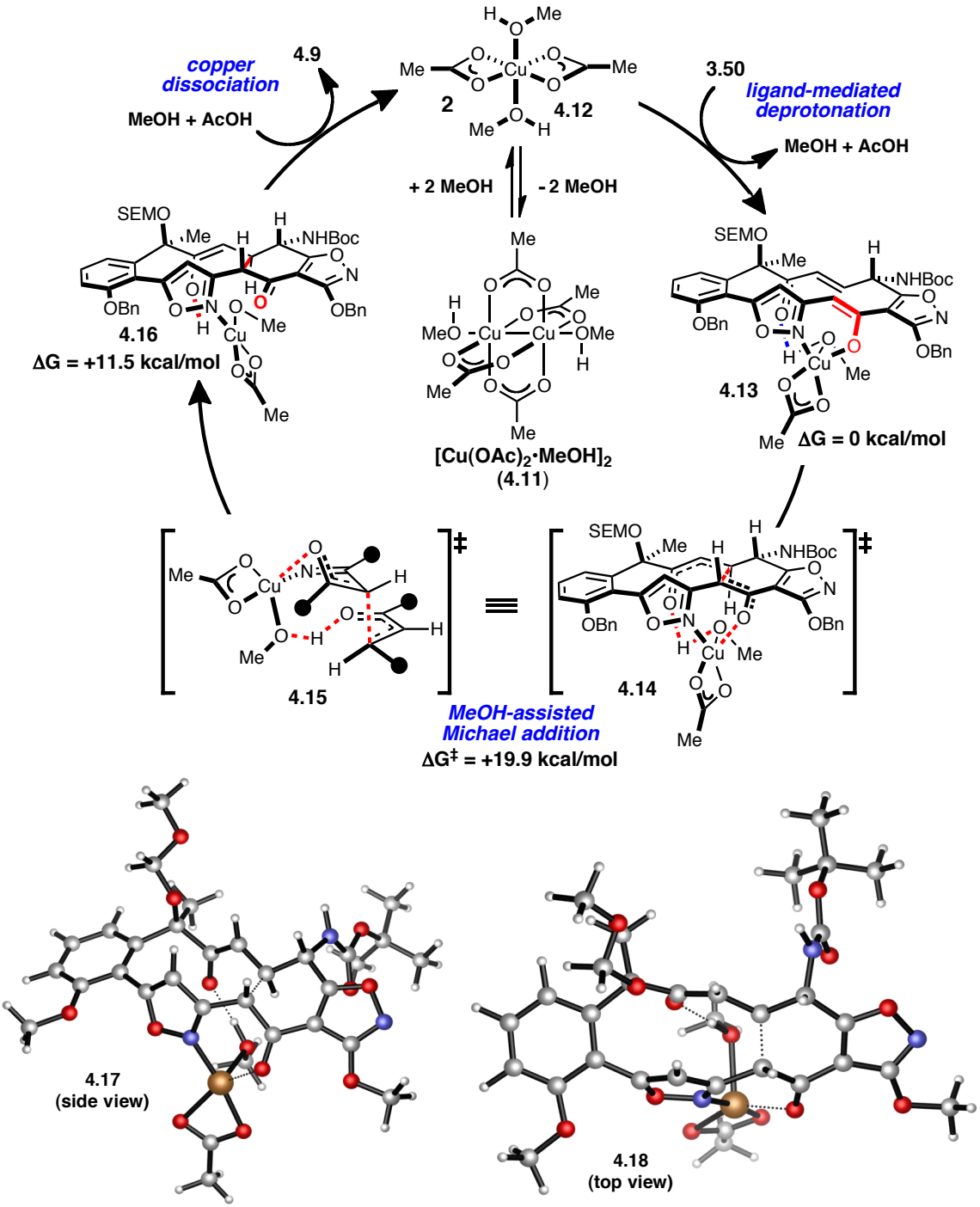


**Figure 4.2** Two views of the computed low energy transition state structure.

[158] It is possible that a second methanol ligand occupies the vacant apical site in **4.13**, however the presence or absence of this ligand is considered inconsequential.

We next turned our attention to the key transition state through which the C4a-C12a carbon-carbon bond forming event occurs. The computed low energy enolate conformer **4.13** proceeds to intermediate **4.16** via an intriguing collection of atomic movements (Figure 4.2).[159] Specifically, as the forming C-C bond compresses the interatomic distance of C4a and C12a, this in turn imparts significant distortion to the C1-carbonyl oxygen bound to copper. To alleviate this forming strain and allow the reacting partners to approach, disassociation of the carbonyl oxygen must also occur in the transition state. Collectively, these movements can be described as a "twist" involving rotation around the nitrogen-copper bond, the breaking of the oxygen-copper bond, and protonation of the forming enolate. The completed operation results in the formation of intermediate **4.16**, which represents the copper-bound enol tautomer of the Michael product. Upon the formation of **4.16**, dissociation of copper may occur with subsequent methanol and acetic acid incorporation. This re-establishes the initial copper species **4.12** and liberates the Michael product.

While this putative mechanism stands to chemical intuition, there are other scenarios that cannot be ruled out in the absence of experimental mechanistic data. For example, a bimetallic mechanism is conceivable since a bimetallic copper complex could enolize the C12a-position while simultaneously activating the enone acceptor. Another possibility is that a second copper complex may activate the enone independent of the copper enolate. However, these two scenarios are unlikely since methanol promotes dissociation of the initial dimeric copper(II) species **4.11**, and the reaction proceeds with

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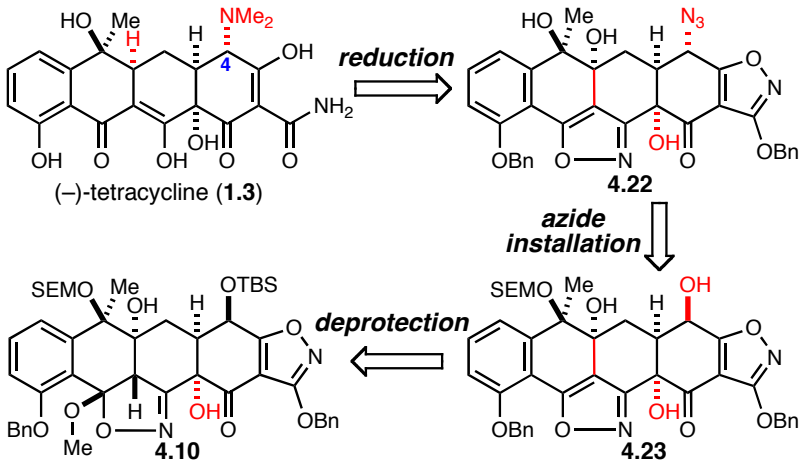
[159] The B3LYP hybrid functional with the 6-31G* (for H, C, O, and N) and MDF10 (for Cu) basis sets were used on truncated derivatives of the macrocycles under scrutiny. M. J. Frisch.; *et al.* Gaussian, Inc.,

only 5 mol % of $Cu(OAc)_2 \cdot H_2O$, making the probability of such reactant aggregation low. A third possibility is that the forming enolate simply deprotonates unactivated methanol from the solvent medium.

**IV. Elaboration of the Cascade Product**

With newfound understanding of the Michael addition, we turned our attention back to the elaboration of the cascade product **4.10** (Scheme 4.9). The most daunting task at this juncture was the installation of nitrogen at C4, which required deprotection of the C4-hydroxyl function and elaboration such that a stereospecific displacement with a nucleophilic nitrogen source may occur. In particular, we worried that elimination of the activated carbinol would outcompete any attempt to displace the leaving group. Once nitrogen is installed and elaborated to the requisite dimethylamine, hydrogenation should yield tetracycline.

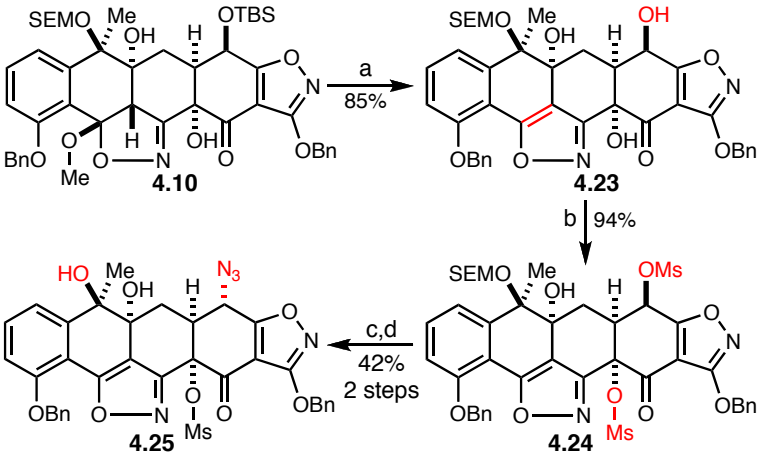
**Scheme 4.9** Transformations required to elaborate **4.10** to tetracycline.




Pittsburgh, PA, 2006. Energy values correspond to computed energies obtained on model system employing truncated protecting groups. See the supporting information for complete details.

Deprotection of the TBS group immediately proved problematic. We were aware that acidic conditions would induce cyclization of the C4-hydroxyl onto the C5a position, which we used to our advantage earlier to determine the presence of a cis ring fusion (*vide supra*), however it was anticipated that judicious selection of an acid with appropriate $pK_a$ value would suppress this undesired reaction. Unfortunately, under a wide variety of conditions, cyclization was facile. Ultimately it was determined that a variant of conditions often used in the context of selective primary TBS group deprotections, HF•pyridine at elevated temperature,[160] facilitated deprotection of the C4-hydroxyl without subsequent cyclization (Scheme 4.10).

**Scheme 4.10** Elaboration of cascade product **4.25**.




Reagents and conditions: (a) 5:2:3 THF:pyr.:HF•pyr., 35 °C; 85%; (b) MsCl, pyr., $CH_2Cl_2$, 35 °C; 94%; (c) $NaN_3$, 2:1 DMF:$H_2O$, rt; (d) 4 *N* HCl, THF, rt; 42% (2 steps).

With secondary carbinol **4.23** in hand, we next looked to functionalize the C4-hydroxyl. Due to the placement of this group on the concave face with respect to the A/B-ring *cis*-decalin, we anticipated that the reactivity might be tempered. Despite this

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[160] Hu, T.; Takenaka, N.; Panek, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 12806-12815.

decreased reactivity, we hoped that the two tertiary carbinols at C12a and C5a would still be significantly less reactive. Unfortunately, treatment of **4.23** with diphenyl phosphorazidate under Mitsunobu[161] or more strongly basic[162] conditions yielded only trace quantities of desired azide due to elimination of the C4-hydroxyl function. Accordingly, a two-step strategy that involved pre-activation of the alcohol, followed by displacement with azide was considered.[163] Yet, treatment of **4.23** with MsCl and pyridine at elevated temperature yielded the bis-mesylated substrate **4.24**. Since mesylation of both alcohols occurs at a similar rate, attempts to differentiate one hydroxyl from another were unsuccessful. Despite this unfortunate lack of selectivity, we attempted azide displacement of mesylate **4.24**, which successfully produced **4.25** after SEM cleavage. Importantly, azide displacement only occurred when a mixed solvent system of DMF and water was employed.

Conformational analysis of the A-ring provided an explanation for the large amount of decomposition observed with both methods used to install the C4-azide (Scheme 4.11). In conformer **4.27**, the C4a-hydrogen atom and C4-substituent are placed in ideal relative positions for an E2-elimination pathway to exist, producing **4.28** (diphenyl phosphorazidate conditions). Accessing conformer **4.29** via ring-flip places the C12a-C4a carbon-carbon bond and the C4a-substituent in ideal alignment for a Grob

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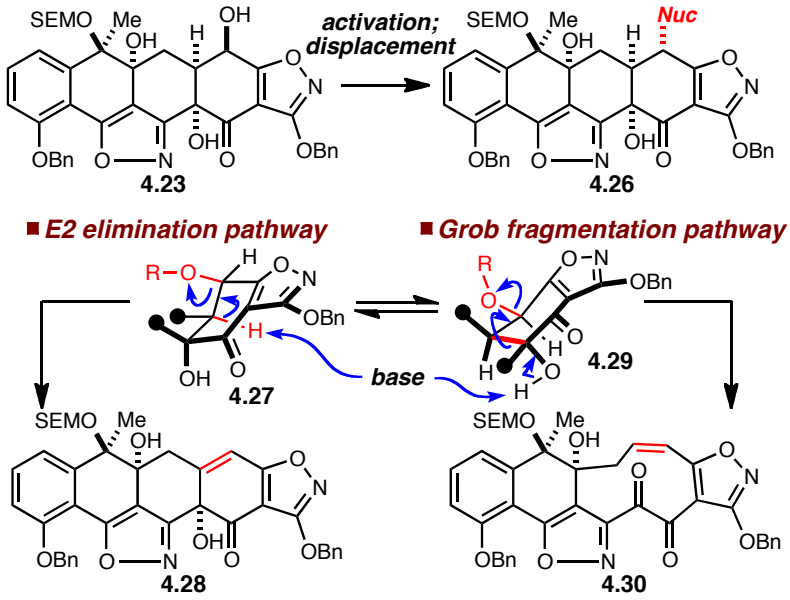
[161] (a) Murai, K.; Morishita, M.; Nakatani, R.; Kubo, O.; Fujioka, H.; Kita, Y. *J. Org. Chem.* **2007**, *72*, 8947-8949. (b) Sze But, T. Y.; Toy, P. H. *Chem. Asian. J.* **2007**, *2*, 1340-1355. (c) Ren, G.-B. *Org. Lett.* **2009**, *11*, 5638-5641. (d) Borisova, S. A.; Guppi, S. R.; Kim, H. J.; Wu, B.; Penn, J. H.; Liu, H.-W.; O'Doherty, G. A. *Org. Lett.* **2010**, *12*, 5150-5153. (e) Wohlfahrt, M.; Harms, K.; Koert, U. *Angew. Chem. Int. Ed.* **2011**, *50*, 8404-8406.

[162] (a) Thompson, A. S.; Humphrey, G. R.; DeMarco, A. M.; Mathre, D. J.; Grabowski, E. J. J. *J. Org. Chem.* **1993**, *58*, 5886-5888. (b) Borodkin, V. S.; van Aalten, D. M. F. *Tetrahedon* **2010**, *66*, 7838-7849.

fragmentation to take place, producing 10-membered macrocycle **4.30** (mesylate displacement conditions). It should be noted that attempted displacement of a C4-mesylate with aqueous dimethylamine resulted in the exclusive formation of the Grob fragmentation product, highlighting the sensitivity of intermediates with activation at this position.

**Scheme 4.11** Different conformers present different decomposition pathways.




## V. Delayed Installation of the Dimethylamine

In light of the difficulties associated with dimethylamine installation prior to hydrogenation, we reconsidered the sequence of events necessary to complete the synthesis (Scheme 4.12). Specifically, we envisioned that the requisite dimethylamine could be installed last, since similar transformations have been achieved within the context of the tetracy-

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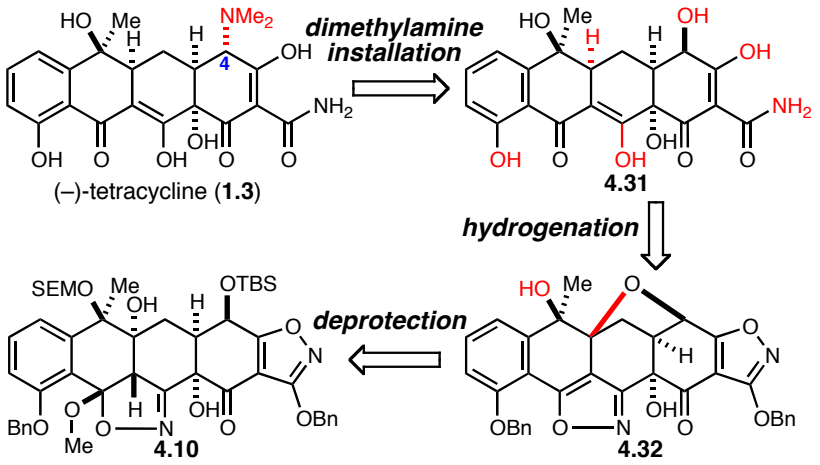
[163] (a) Nie, L.-D.; Shi, X.-X.; Ko, K. H.; Lu, W.-D. *J. Org. Chem.* **2009**, *74*, 3970-3973. (b) Hanessian, S.; Vakiti, R. R.; Dorich, S.; Banerjee, S.; Lecomte, F.; DelValle, J. R.; Zhang, J.; Deschênes-Simard, B. *Angew. Chem. Int. Ed.* **2011**, *50*, 3497-3500.

clines when the C4-position is at a ketone oxidation state.[164] Thus, deprotection of the cascade product **4.10** followed by hydrogenation should yield **4.31**, the highly functionalized 4-hydroxy-4-dedimethylaminotetracycline. Of course, this revised synthesis plan relies heavily upon the successful hydrogenation cascade, something that has not been validated in any form to this point. This strategy was particularly appealing at this juncture since intermediate **4.31** is a putative degradation product of tetracycline.[165] Therefore, structural confirmation could be achieved in the event that the final dimethylamine installation is fraught with difficulty. This safeguard, coupled with our knowledge regarding the difficulty of C4-hydroxyl functionalization, justified the implementation of this revised strategy.

**Scheme 4.12** Revised endgame strategy towards (–)-tetracycline.



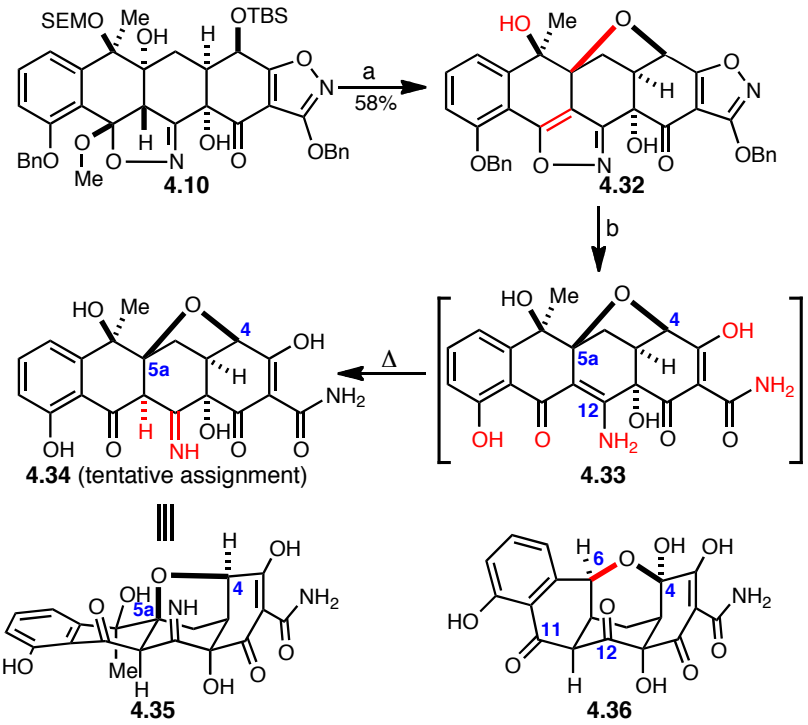

[164] (a) Blackwood, R. K.; Stephens, C. R. *J. Am. Chem. Soc.* **1964**, *86*, 2736-2737. (b) Gurevich, A. I.; Karapetyan, M. G.; Kolosov, M. N. *Khim. Prir. Soedin.* **1970**, *6*, 247-251.

[165] (a) Blackwood, R. K.; Stephens, C. R. *Can. J. Chem.* **1965**, *43*, 1382-1388. (b) Blackwood, R. K.; Ferry, G.; Stephens, C. R. 4-Dedimethylaminatetracycline and 5a,6-Anhydro derivatives thereof. U. S. Patent 3,159,675, Nov. 23, 1971. (c) Gu, J.; Cai, P.; Gong, Y.; Ruppen, M. E.; Storz, T. *J. Antibiot.* **2010**, *63*, 693-698.

Elaboration of **4.10** commenced via an initial deprotection reaction under strong acid conditions similar to those established previously in the synthesis of **3.55** (Scheme 4.13). These conditions furnished the polycyclic structure **4.32** in good yield for the overall transformation. Spectral comparison of both **3.55** and **4.32** reveals expected homology between the two diastereomeric compounds (Figure 4.3). Unfortunately, hydrogenation of **4.32** did not produce **4.31** as was anticipated, due to the inability of the reduced isoxazole to eject the C5a-oxygen atom. Thus, **4.33** was produced as the immediate product of the reaction, which is postulated to slowly tautomerize to imine **4.34** upon warming. Conformational analysis of this polycyclic intermediate revealed that the three dimensional structure is remarkably similar to "tetracycloxide" derivatives containing a C11-C12-diketone.[166] One such tetracycloxide, **4.36**, is depicted in Scheme 4.13. Unfortunately, attempts to hydrolyze the enaminone present within **4.33** under acidic conditions (HCl, AcOH, or PTSA) failed to produce the desired C12-oxygenated compound. Further, both **4.33** and **4.34** decomposed rapidly upon isolation, rendering them unuseful as intermediates for the synthesis.

[166] Esse, R. C.; Lowery, J. A.; Tamorria, C. R.; Sieger, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 3874-3875.

**Scheme 4.13** Elaboration of cascade product **4.10** via polycycle **4.32.**




Reagents and conditions: (a) 4 *N* HCl, THF, 35 °C; 58%; (b) $H_2$, Pd(black), 4:1 dioxane:$H_2O$, rt.

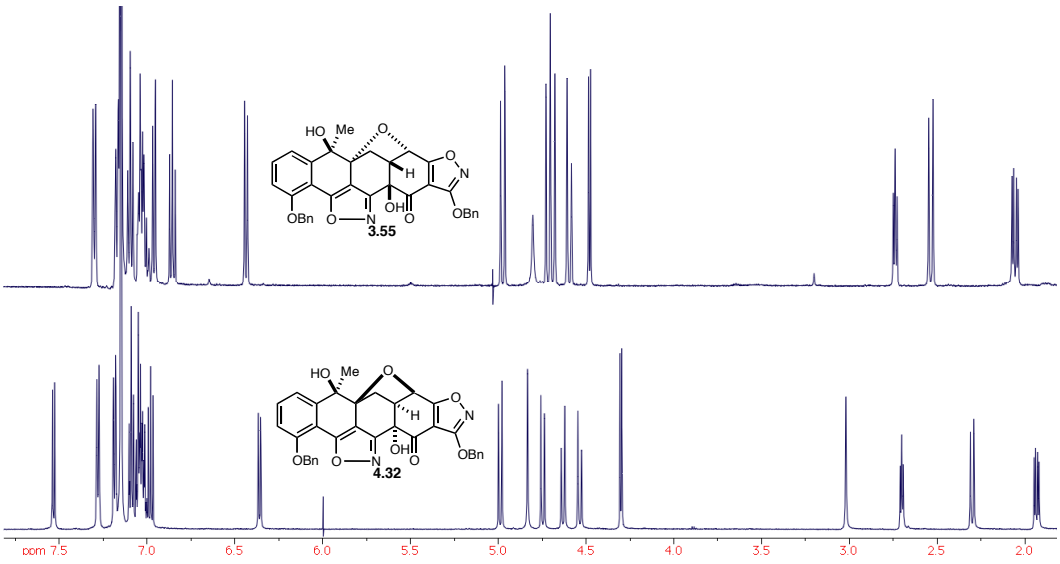
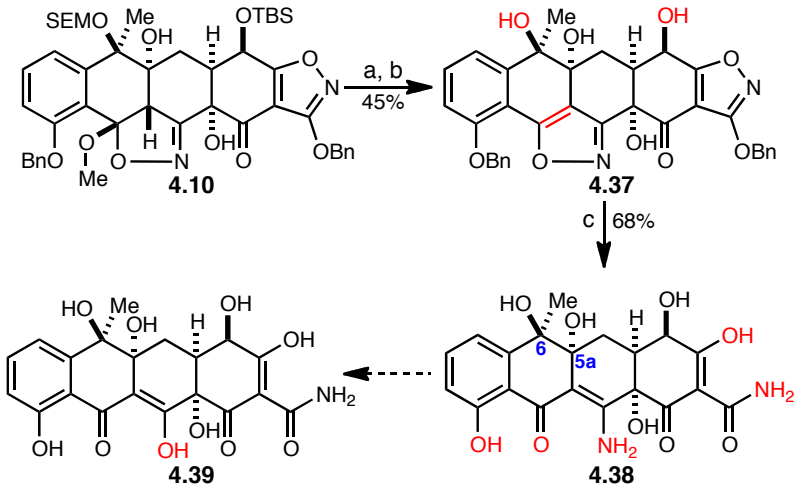



**Figure 4.3** $^1$H NMR spectral comparison of polycycle **3.55** (upper) and **4.32** (lower) in $d_6$-DMSO.

While the deprotection/cyclization cascade used to transform **4.10** to **4.32** was viewed initially as an ideal way to deprotect the C4- and C6-hydroxyl functions, the tetrahydrofuran formed during the reaction proved to be counter-productive in the subsequent hydrogenation step. Thus, we revisited cascade product **4.10** in an attempt to ascertain whether this compound could be deprotected without C4-C5a cyclization (Scheme 4.14). Indeed, less forcing conditions involving exposure of **4.10** to 6 *N* HCl at room temperature rather than 35 °C facilitated the selective deprotection of the C6-hydroxyl function. Subsequent cleavage of the TBS protecting group with HF•pyr. at elevated temperature afforded **4.37** in good yield for the two steps. Gratifyingly, this compound underwent efficient hydrogenation, which enabled the cleavage of both isoxazoles and the remaining benzyl ether to yield **4.38** in 68% yield. Similar to the hydrogenation using polycycle **4.32** as substrate, C5a-reduction was not observed in the present case.

**Scheme 4.14** Synthesis of advanced intermediate **4.38**.




Reagents and conditions: (a) 6 *N* HCl, THF, rt; (b) 5:2:6 THF:pyr.:HF•pyr., 30 ºC; 45% (2 steps); (c) $H_2$, Pd(black), 4:1 dioxane:$H_2O$, rt; 68%.

Unfortunately the enaminone function present in both **4.38** was exceedingly resistant to acid hydrolysis. It was anticiated that a substrate with a reduced C5a-position would not be an ideal substrate for several reasons. First, reduction of this position im-

parts significant acid sensitivity to the molecule since the C-ring may now aromatize via elimination of the C6-hydroxyl function. Secondly, precedent by Suzuki and co-workers in the context of the synthesis of *ent*-seragakinone A (**4.41**) demonstrated the acid hydrolysis was not feasible in their system, forcing implementation of diazotization to effect this transformation (Scheme 4.15).[167,168] Yet, **4.38** was considered a substrate with a very different reactivity profile, since acid-mediated ejection of the C5a-hydroxyl function is entirely reasonable.[169] Since ionization of **4.38** is considered a facile process, it was hypothesized that molecule may extrude water to produce imine **4.42** *in situ*. Due to this reactivity, hydrolysis was presumed to be feasible, however no exchange was observed under a variety of conditions (AcOH/$H_2O$, PTSA/$CH_3CN$/$H_2O$, 1 *N* HCl/THF, 0.1 M pH 2 glycine•HCl buffer, Amberlyst$^{TM}$ 15 resin/$CH_3CN$/$H_2O$).

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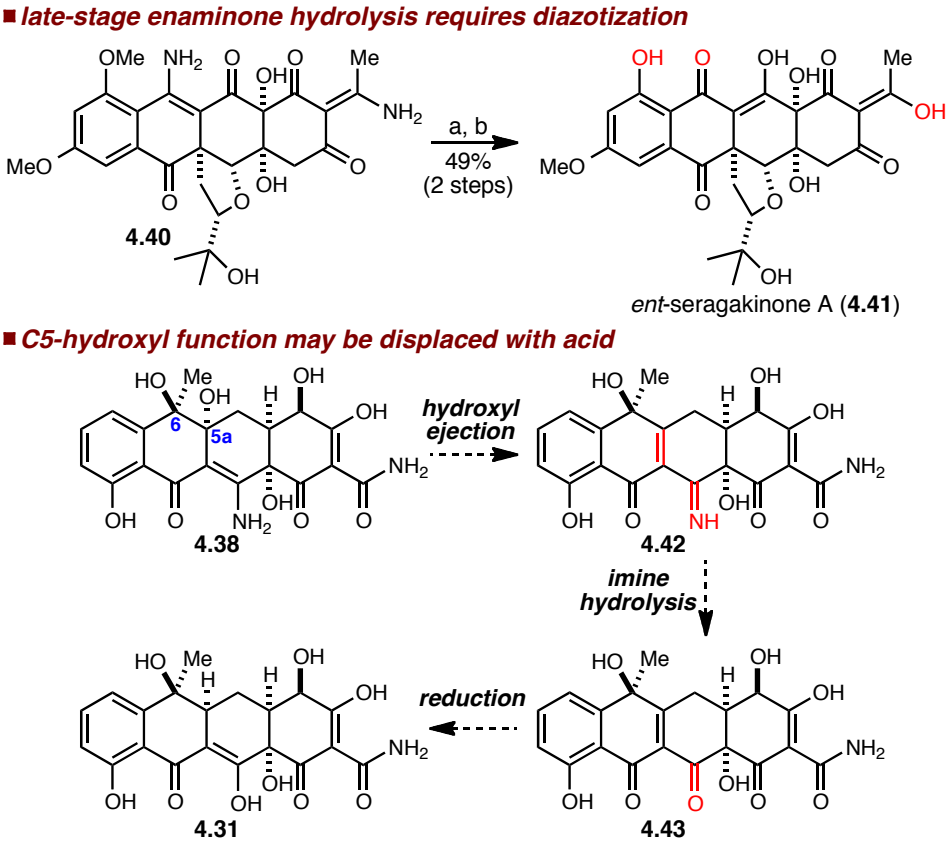
[167] Takada, A.; Hashimoto, Y.; Takikawa, H.; Hikita, K.; Suzuki, K. *Angew. Chem. Int. Ed*. **2011**, *50*, 2297-2301.

[168] While these conditions could be applied to our system, it is unlikely that we could activate the enaminone without also diazotizing the amide at C2. This was not a problem in the seragakinone A synthesis since both enaminones needed to be hydrolyzed.

[169] ESI of **4.38** results in a major ion that represents loss of water. This compound is the first in the synthesis to show this behavior during ionization, implying that the C5a-hydroxyl function is easily extruded.

**Scheme 4.15** Hydrolysis of the enaminone function in both the context of *ent*-seragakinone A and proposed hydolysis of substrate **4.38**.

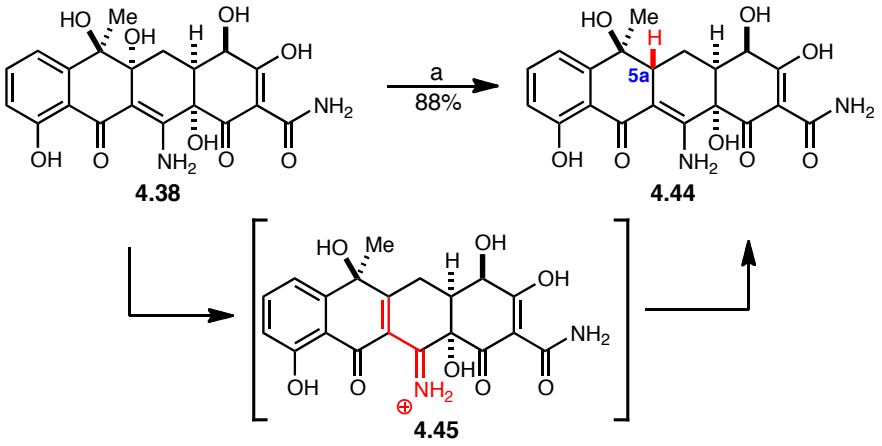



Reagents and conditions: (a) *t*-BuONO, $CF_3CO_2H$, DMSO, rt; 1 M NaOH, rt; (b) NaI, $CeCl_3 \cdot 7H_2O$, $CH_3CN$, reflux; 49% (2 steps).

To this point in the synthesis, our structural determinations were made on the basis of both coupling constant and nOe data. However, due to the lack of reactivity associated with enaminone hydrolysis, it was felt that more rigorous structural evidence was needed in order to be certain that our problematic hydrolysis was a manifestation of substrate stability rather than structural inconsistency. Fortuitously, validation of both our gross carbocyclic structure and relative stereochemistry obtained from the Cu(II)/Ce(III) cascade arose during attempts to effect a reduction of the C5a-position (Scheme 4.16). During these studies, we found that **4.38** is cleanly reduced to **4.44** in the presence of $NaBH_3CN$ and acetic acid, presumably via intermediate **4.45**. Unfortunately, while the reduction was stereoselective, the wrong stereocenter was produced at the C5a-position.

We postulate that the C6-methyl group most likely stabilizes the iminium via hyperconjugation, thus increasing steric interactions on the back face of the molecule.

**Scheme 4.16** Reduction of the C5a-position.




Reagents and conditions: (a) $NaBH_3CN$, AcOH, $CH_3CN$, 30 ºC; 88%.

Despite this unfortunate stereochemical outcome, the production of **4.44** was welcomed due to the crystallinity of the compound. Specifically, a saturated solution of **4.44** in diethylether produced crystals of appropriate uniformity and size for X-ray diffraction. The X-ray crystal structure of **4.44** is depicted in Figure 4.4. While this compound reveals the nature of the C5a-stereogenic center, it also reveals the relative stereochemistry of the remaining stereocenters as well. Gratifyingly, each of the stereocenters implicated in the reaction cascade are of the expected orientation, thus validating not only the intermediate structures themselves, but also the logic used to justify decisions made at critical junctures within the synthesis.

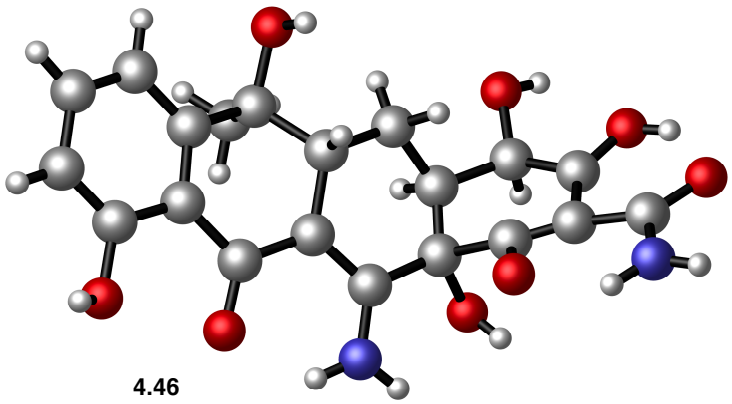



**Figure 4.4** X-ray crystal structure of **4.44**.

## VI. Conclusion

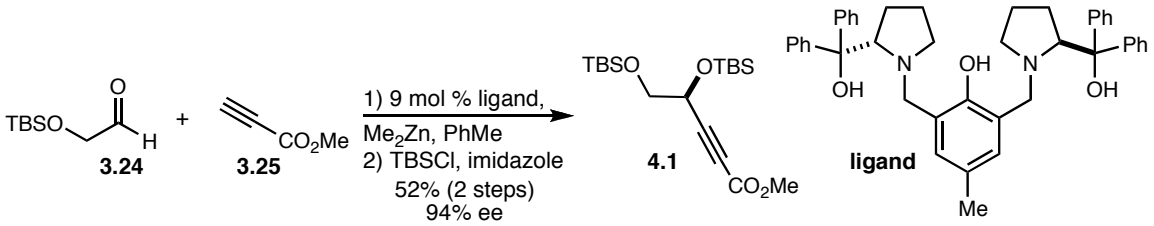
The results detailed in this chapter describe the successful execution of a transannular cascade to produce both the carbocyclic framework of (–)-tetracycline and the correct stereochemistry at the C4a- and C12a-positions. This cascade represents the end result of critical analysis of the stereochemical interplay between the five stereogenic centers that comprise tetracycline. Further, a mechanism for the Michael reaction was proposed that explains the unique ability for copper(II) to facilitate the key Michael addition. Unfortunately, complete elaboration of the cascade product to (–)-tetracycline was not achieved, ultimately leaving the project unfinished. Despite this unfortunate outcome, we hope that the coupling of computational and experimental chemistry, as described in this thesis, will serve as a guide for others who wish to utilize macrocyclic stereocontrol in synthesis endeavors. Indeed, without computational insight into otherwise puzzling experimental outcomes, the path forward would have been less clear. Further, we hope that the potential for facile transmission of stereochemical information from one position to another within a macrocyclic setting has been demonstrated. Thus, with rationally designed mac-

rocycles adorned with appropriate functionality, a wide array of polycyclic structures can be targeted.

# *Chapter 4*

## VII. Experimental Section

### A. Experimental Procedures




**(*S*)-methyl 5-(*tert*-butyldimethylsilyloxy)-4-hydroxypent-2-ynoate (4.1).** To a flame-dried 5 L 3-necked flask under an atmosphere of argon, **ligand**[170] (13.1 g, 20.5 mmol, 9 mol %) was added, followed by toluene (1.14 L, 0.20 M wrt to **3.24**). Next, methyl propiolate **3.25** (60.9 mL, 0.684 mol, 3.00 equiv.) was added rapidly via syringe. This slightly yellow solution was then cooled to –15 °C, and dimethylzinc (0.570 L of a 1.2 M solution in toluene, 0.684 mmol, 3.00 equiv.) was added via cannula to the solution (caution, gas evolution). Next, aldehyde **3.24** (39.7 g, 228 mmol, 1.00 equiv.) in toluene (18

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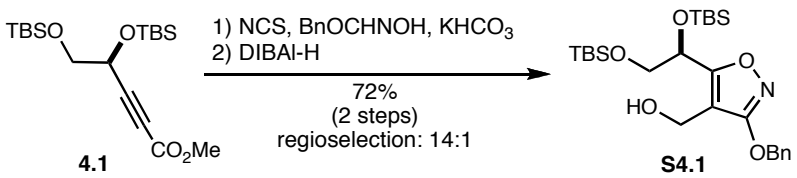
[170] (a) Trost, B. M.; Weiss, A. H.; von Wangelin, A. J. *J. Am. Chem. Soc.* **2006**, *128*, 8-9. (b) Trost, B. M.; Weiss, A. H. *Org. Lett.* **2006**, *8*, 4461-4464.

mL, 13 M) at room temperature was added directly to the cooled reaction via syringe pump over 36 h. During this addition, the internal temperature of the reaction was held between –11 and –10.5 °C. The reaction was then allowed to stir an additional 8 h, upon which time it was quenched carefully via addition of sat. $NH_4Cl$ (caution, gas evolution) and extracted three times with $Et_2O$. The combined organic extracts were washed once with water, dried with $Na_2SO_4$ and concentrate *in vacuo*. The crude material was purified via flash chromatography on silica gel (pure hexanes → 8:1 → 6:1 hexanes:EtOAc) affording the intermediate propargylic alcohol (45.2 g, 77% yield, 94% ee) as a slightly yellow liquid that was ca. 95% pure via NMR.

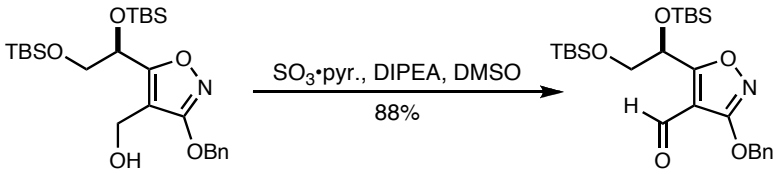
To a solution of the intermediate propargylic alcohol (45.2 g, 178 mmol, 1.00 equiv.) in DMF (350 mL, 0.50 M) at 0 °C under an atmosphere of nitrogen, imidazole (18.2 g, 0.267 mol, 1.5 equiv.) was added in a single portion, followed TBSCl (28.2 g, 187 mmol, 1.05 equiv.) also in a single portion. The reaction was stirred for 3.5 h, upon which time it was quenched with water and extracted three times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography (19:1 hexanes:EtOAc) affording **4.1** (44.0 g, 66%) as a colorless liquid. Overall yield for the two steps: 52%. The spectroscopic information matched that of **3.26** reported previously with the exception of optical rotation, which was opposite to that reported previously (*vide supra*).




**(*R*)-(3-(benzyloxy)-5-(2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecan-5-yl)isoxazol-4-yl)methanol (S4.1).** To a solution of **4.1** (44.0 g, 118 mmol, 1.00 equiv.) in EtOAc (590 mL, 0.20 M) at room temperature exposed to air, BnOCHNOH (17.8 g, 118 mmol, 1.00 equiv.) was added, followed by the addition of $KHCO_3$ (118 g, 1.18 mol, 10.0 equiv.) and NCS (15.8 g, 118 mmol, 1.00 equiv.). The flask was fitted with a reflux condensor, and the suspension was heated to 48 °C under an atmosphere of nitrogen for 12 h. The reaction was treated with an additional 1.00 equiv. of oxime and NCS every 12 h for a total 9 additions or 9 equiv. of each. The resulting cloudy and slightly yellow mixture was passed through filter paper and concentrated *in vacuo*. The resulting crude residue was suspended in hexanes, poured into a separatory funnel, and washed with water. The resulting emulsion was treated with methanol, inducing a yellow liquid to fall to the bottom of the funnel. This material was removed discarded, and the procedure repeated two more times. The resulting pale yellow organic layer was dried with $Na_2SO_4$ and concentrated *in vacuo*. This crude material was purified via flash chromatography on silica gel (pure hexanes → 8:1 hexanes:EtOAc) affording the intermediate isoxazole (58.6 g, 95% yield, 14:1 regioselectivity) as a slightly yellow liquid.

To a solution of the intermediate isoxazole (29.8 g, 57.1 mmol, 1.00 equiv.) in toluene (190 mL, 0.30 M) at –78 °C under an atmosphere of nitrogen, DIBAl-H (117 mL of a 1.0 M solution in toluene, 171 mmol, 3.00 equiv.) at –78 °C was added against the side of the flask over 10 minutes via cannula. The resulting slightly yellow solution was

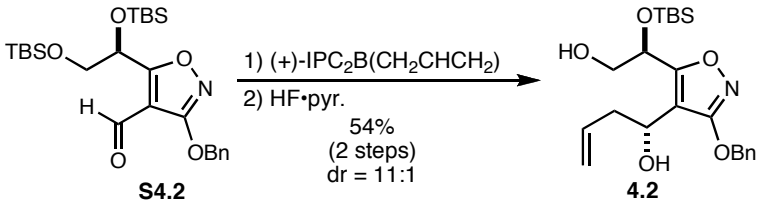
stirred at –78 °C for 2 h, upon which time it was carefully quenched with a 20% w/v solution of Rochelle's salt. The reaction was then warmed to room temperature while stirring vigorously for 3 h. The biphasic mixture was extracted three times with EtOAc, the combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (10:1 hexanes:EtOAc) affording **S4.1** (21.3 g, 76%) as a clear liquid. The spectroscopic information matched that of **S3.2** reported previously with the exception of optical rotation, which was opposite to that reported previously (*vide supra*). Yield for the two steps: 72%.




**S4.1** **S4.2**

**(*R*)-3-(benzyloxy)-5-(2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecan-5-yl)isoxazole-4-carbaldehyde (S4.2).** To a solution of **S4.1** (20.5 g, 41.5 mmol, 1.00 equiv.) in $CH_2Cl_2$ (100 mL, 0.40 M) at 0 °C under an atmosphere of nitrogen, DMSO (24 mL, 1.7 M) was added followed by DIPEA (21.3 mL, 125 mmol, 3.00 equiv.). To a second flask, DMSO (42 mL, 2.0 M wrt $SO_3$•pyr.) was added, followed by $SO_3$•pyr. (13.2 g, 83.0 mmol, 2.00 equiv.). This mixture was stirred for 5 minutes upon which time most solid had dissolved. Next, the $SO_3$•pyr. solution was added to the solution containing **S4.1** rapidly via syringe. The resulting clear and slightly brown mixture was stirred for one hour at 0 °C, upon which time the reaction was placed under reduced pressure, and the $CH_2Cl_2$ was removed *in vacuo* on a rotovap with the bath temperature set to 29 °C. The

remaining solution was poured directly onto a silica gel column and purified via flash chromatography (15:1 hexanes:EtOAc) affording **S4.2** (17.9 g, 88%) as a clear liquid. The spectroscopic information matched that of **S3.3** reported previously with the exception of optical rotation, which was opposite to that reported previously (*vide supra*).



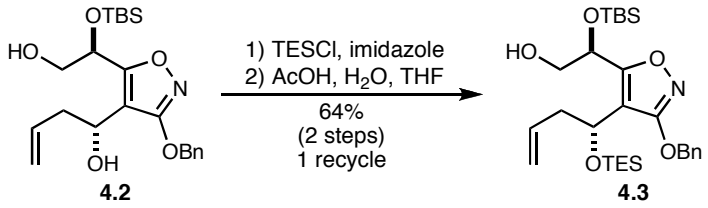

**3-(benzyloxy)-5-((*R*)-8,8-diethyl-2,2,3,3-tetramethyl-4,7-dioxa-3,8-disiladecan-5-yl)-4-((*S*)-1-(triethyl-silyloxy)but-3-enyl)isoxazole (4.2).** To a solution of (+)-$IPC_2B(CH_2CHCH_2)$[171] (66.6 mL of a 1.0 M solution in pentane, 66.6 mmol, 1.30 equiv.) in diethylether (128 mL, 0.52 M wrt reagent) at –110 °C under an atmosphere of nitrogen, **S4.2** (25.2 g, 51.2 mmol) in $Et_2O$ (128 mL, 0.40 M) at –78 °C was added along the side of the flask via cannula over ten minutes. The resulting solution was slowly warmed to –78 °C over 5 minutes, during which time the slightly yellow solution became mostly clear. The reaction was stirred at –78 °C for one hour, upon which time it was warmed directly to 0 °C, and a premixed solution of 2:1 2 *N* NaOH : 30% aq. $H_2O_2$ (256 mL) at room temperature was added portionwise. The reaction was then stirred vigorously for 15 minutes at 0 °C, upon which time the cooling bath was removed, and the cloudy mix-

[171] (a) Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1987**, *52*, 320-322. (b) Brown, H. C.; Bhat, K. S.; Randad, R. S. *J. Org. Chem.* **1989**, *54*, 1570-1576.

ture was stirred for an additional 2 h. The resulting solution was extracted three times with hexanes, the combined organic extracts were then dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude liquid was purified via flash chromatography on silica gel (15:1 hexanes:EtOAc) affording the intermediate homoallylic alcohol (29.9 g, 11:1 dr) as a colorless liquid that was ca. 85% pure by NMR.

To a solution of 5:2:1 THF:pyr.:HF•pyr. (154 mL, 3 ml solution/mmol sm) at 0 °C in a plastic bottle exposed to air, the intermediate alcohol (29.9 g, ca. 51.2 mmol) in THF (171 mL, 0.30 M) was added rapidly. The flask was washed three times with 5 mL THF, and these washings were also added to the reaction mixture. The reaction was stirred for 10 minutes at 0 °C, upon which time the cooling bath was removed. After 2.5 h of stirring at room temperature, the solution was quenched with sat. $NaHCO_3$ (caution, gas evolution). The resulting mixture was extracted three times with $CH_2Cl_2$. The combined organic extracts were washed once with brine, dried with $Na_2SO_4$, and concentrated *in vacuo*. The crude liquid was purified via flash chromatography on silica gel (10:1 → 4:1 → 2:1 hexanes:EtOAc) affording **4.2** (11.5 g) as a slightly pink liquid. Yield for the two steps: 54%. This compound was characterized as a 5.7:1 ratio of diastereoisomers. $\boldsymbol{R_f}$ = 0.52 (2:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = +39 (*c* 0.85, $CHCl_3$); **IR** (neat) 3387, 2930, 2857, 1639, 1509, 1462, 1363, 1256, 1111, 1058, 985, 838, 780; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.23 (d, 2H), 7.08 (t, *J* = 7.6, 6.3, 1.6 Hz, 2H), 7.05 – 7.00 (m, 1H), 5.77 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.19 (s, 2H), 5.05 – 4.96 (m, 3H), 4.74 (dt, *J* = 7.8, 6.0 Hz, 1H), 3.74 (td, *J* = 6.0, 3.6 Hz, 2H), 3.22 (d, *J* = 5.9 Hz, 1H), 2.79 – 2.62 (m, 3H), 0.89 (s, 9H), 0.03 (d, *J* = 6.3 Hz, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 169.82, 168.57, 136.36, 134.73,

128.73, 128.51, 128.42, 118.07, 109.87, 71.97, 69.38, 65.81, 64.84, 41.64, 25.97, 18.41, -4.72, -5.01; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 420.2201; found: 420.2209 (ESI).

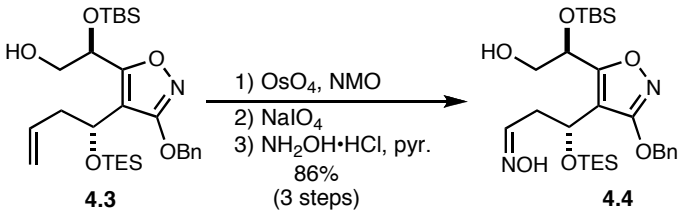



**4.2** **4.3**

**(*R*)-2-(3-(benzyloxy)-4-((*R*)-1-(triethylsilyloxy)but-3-enyl)isoxazol-5-yl)-2-(*tert*-butyldimethylsilyloxy)ethanol (4.3).** To a solution of **4.2** (11.5 g, 27.4 mmol, 1.00 equiv.) in DMF (137 mL) at 0 °C under an atmosphere of nitrogen, imidazole (5.60 g, 82.2 mmol, 3.00 equiv.) was added, followed by TESCl (9.63 mL, 57.5 mmol, 2.10 equiv.) over 1 minute. The resulting clear solution was stirred at room temperature for 20 minutes, upon which time it was quenched with $H_2O$, and extracted three times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The residue was purified via flash chromatography on silica gel (20:1 hexanes:EtOAc) affording the intermediate tris-silylether (15.0 g, 84%) as a colorless liquid.

To the tris-silylether (14.8 g, 22.8 mmol, 1.00 equiv.) at room temperature exposed to air, a 3:3:10 mixture of AcOH:$H_2O$:THF (76 mL, 0.30 M) was added rapidly. The turbid mixture was allowed to stir at room temperature for 9 h, upon which time it was quenched with sat. $NaHCO_3$ and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The resulting liquid was purified via flash chromatography on silica gel (20:1 → 8:1 hexanes:EtOAc) affording

**4.3** (4.67 g, 38%) and starting material **4.2** (7.39 g, 50%), both as colorless liquids. The starting material was resubjected to the above conditions, yielding a total of 4.62 g of **4.3** (76%) as a colorless liquid. Overall yield for the two steps: 64%. This compound was characterized as a 4.7:1 ratio of diastereoisomers (obtained from a previously unoptimized procedure). $R_f$ = 0.24 (10:1 hexanes:EtOAc); $[\alpha]_D$ = +23 (*c* 0.35, $CHCl_3$); **IR** (neat) 3437, 2954, 2878, 1639, 1509, 1461, 1360, 1255, 1082, 1005, 951, 914, 837, 779; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.32 – 7.20 (m, 2H), 7.14 – 7.05 (m, 2H), 7.05 – 6.99 (m, 1H), 5.81 – 5.70 (m, 1H), 5.20 (s, 2H), 5.14 (t, *J* = 6.1 Hz, 1H), 5.09 – 4.94 (m, 1H), 4.85 (t, *J* = 6.8 Hz, 1H), 3.88 (t, *J* = 6.4 Hz, 1H), 2.82 – 2.54 (m, 2H), 2.17 (t, *J* = 6.6 Hz, 1H), 1.05 – 0.84 (m, 18H), 0.67 – 0.49 (m, 6H), 0.08 (d, *J* = 3.9 Hz, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 169.74, 168.60, 136.44, 134.57, 128.65, 128.61, 128.52, 117.91, 109.23, 71.89, 69.69, 65.87, 65.58, 43.36, 25.98, 18.44, 7.05, 5.15, -4.53, -4.85; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 534.3066; found: 534.3071 (ESI).



**4.3** **4.4**

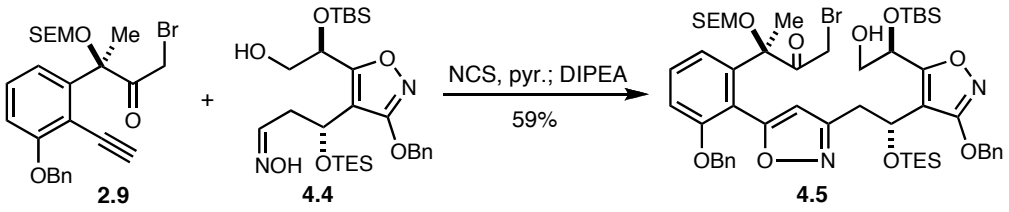
**(*S*)-3-(3-(benzyloxy)-5-((*R*)-1-(*tert*-butyldimethylsilyloxy)-2-hydroxyethyl)isoxazol-4-yl)-3-(triethylsilyloxy)propanal oxime (4.4).** To a solution of **4.3** (4.42 mg, 8.28 mmol, 1.00 equiv.) in 1:1:1 acetone:pH 7 phosphate buffer:THF (28 mL total, 0.30 M) at room temperature exposed to air, NMO (1.46 g, 12.4 mmol, 1.50 equiv.) was added, followed by $OsO_4$ (2.07 mL of a 2.5 wt% solution in water, 0.025 equiv.). The reaction was

stirred for 5.5 h at room temperature, upon which time it was cooled to 0 °C and a sat. $NaHCO_3$ solution (20 mL) containing 2 g $NaHSO_3$ was added. The reaction quickly turned brown after this addition. The cooling bath was removed, and the reaction was stirred for 7 minutes. The resulting mixture was diluted with $H_2O$ (10 mL) and extracted three times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* to afford a brown foam.

The intermediate diol was immediately dissolved in a 3:1 mixture of THF:pH 7 phosphate buffer (33 mL total, 0.25 M) at room temperature exposed to air, and $NaIO_4$ (7.08 g, 58.6 mmol, 4.00 equiv.) was added in a single portion. The reaction soon became cloudy upon this addition. After stirring for 12 minutes at room temperature, the reaction was diluted with $H_2O$ and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* affording a brown foam.

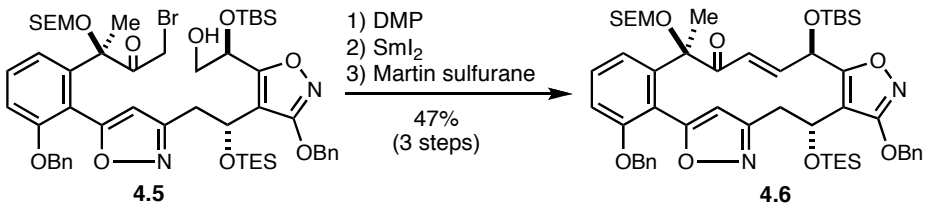
The intermediate aldehyde was dissolved in absolute ethanol (28 mL, 0.30 M) and cooled to 0 °C under an atmosphere of nitrogen. Next, pyridine (8.3 mL, 1.0 M wrt **4.3**) was added followed by hydroxylamine hydrochloride (2.29 g, 33.1 mmol, 4.00 equiv.). The resulting solution was stirred for 2.5 h, upon which time the reaction was quenched at 0 °C with sat. $NH_4Cl$. The resulting mixture was then diluted with $H_2O$, and extracted three times with $Et_2O$. The combined organic extracts were then dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via MPLC (10% → 50% EtOAc and hexanes) affording **4.4** (3.92 g, 86%) as a white foam and a ca. 1:1 mixture of *E* and *Z* oxime isomers. Yield for the three steps: 86%. $\boldsymbol{R_f}$ = 0.59 (2:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = +24 (*c* 3.2, $CHCl_3$); **IR** (neat) 3329, 2956, 2879, 1638, 1509, 1459, 1359, 1256, 1098, 1005,

949, 837.8, 745, 696; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 9.14 (s, 1H), 8.71 (s, 1H), 7.44 – 7.35 (m, 1H), 7.34 – 7.25 (m, 4H), 7.19 – 7.08 (m, 6H), 7.05 (td, *J* = 7.3, 1.5 Hz, 2H), 6.80 (t, *J* = 5.4 Hz, 1H), 5.31 – 5.17 (m, 4H), 5.09 (t, *J* = 6.8 Hz, 1H), 4.99 (t, *J* = 6.6 Hz, 1H), 3.99 – 3.86 (m, 4H), 3.16 (ddd, *J* = 15.1, 6.8, 5.4 Hz, 1H), 2.97 (dddd, *J* = 15.1, 6.7, 5.5, 1.2 Hz, 1H), 2.85 – 2.64 (m, 2H), 1.02 – 0.84 (m, 36H), 0.65 – 0.48 (m, 12H), 0.10 (d, *J* = 6.6 Hz, 12H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 169.71, 169.60, 168.79, 168.76, 148.24, 148.19, 136.38, 128.74, 128.70, 128.65, 128.57, 128.55, 128.49, 109.11, 108.87, 72.09, 72.03, 69.75, 69.67, 65.87, 65.82, 63.92, 62.95, 38.89, 34.59, 26.12, 26.02, 18.49, 7.01, 5.11, 5.04, 5.03, -4.51, -4.54, -4.79; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 551.2967; found: 551.2961(ESI).




**(*R*)-3-(3-(benzyloxy)-2-(3-((*R*)-2-(3-(benzyloxy)-5-((*R*)-1-(*tert*-butyldimethylsilyl-oxy)-2-hydroxyethyl)-isoxazol-4-yl)-2-(triethylsilyloxy)ethyl)isoxazol-5-yl)phe-nyl)-1-bromo-3-((2-(trimethylsilyl)ethoxy)me-thoxy)butan-2-one (4.5).** To a solution of **2.9** (3.28 g, 6.51 mmol, 1.20 equiv.) and **4.4** (3.04 g, 5.52 mmol, 1.00 equiv.) in $CHCl_3$ (110 mL, 0.050 M) at room temperature under an atmosphere of nitrogen, pyridine (0.089 mL, 1.1 mmol, 0.20 equiv.) was added, followed by NCS (774 mg, 5.80 mmol, 1.05 equiv.). The reaction was stirred at room temperature for 20 minutes, upon which time a reflux condensor was fitted to the flask, and the reaction was heated to 40 °C.

Next, DIPEA (3.78 mL, 22.1 mmol, 4.00 equiv.) in chloroform (21 mL) was added directly to the solution over 25 h via syringe pump. The resulting orange/yellow solution was then heated to 50 °C for an additional 19 h. The reaction was then diluted with water and extracted three times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via MPLC (5% → 40% EtOAc and hexanes) affording **4.5** (3.40 g, 59% yield) as a slightly yellow foam that was ca. 95% pure by NMR. $\boldsymbol{R_f}$ = 0.52 (4:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = +12 (*c* 1.2, $CHCl_3$); **IR** (neat) 3432, 2954, 2879, 1740, 1612, 1577, 1510, 1454, 1361, 1250, 1067, 1005, 837, 744, 696; **$^1$H NMR** (600 MHz, $C_6D_6$) δ 7.34 – 7.28 (m, 2H), 7.13 – 6.99 (m, 8H), 6.97 – 6.88 (m, 2H), 6.51 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.17 (s, 1H), 5.38 (t, *J* = 7.0 Hz, 1H), 5.20 (dd, *J* = 7.4, 4.8 Hz, 2H), 4.71 – 4.59 (m, 2H), 4.41 (m, 2H), 4.34 – 4.19 (m, 2H), 4.01 – 3.87 (m, 2H), 3.63 (td, *J* = 9.4, 6.7 Hz, 1H), 3.49 (d, *J* = 7.1 Hz, 1H), 3.30 (td, *J* = 9.5, 7.0 Hz, 1H), 2.40 (dd, *J* = 7.1, 6.2 Hz, 1H), 1.70 (s, 3H), 0.93 (m, 18H), 0.80 (ddd, *J* = 9.1, 6.6, 3.4 Hz, 2H), 0.61 (qd, *J* = 7.9, 2.7 Hz, 6H), 0.12 (d, *J* = 9.6 Hz, 6H), -0.03 (d, *J* = 1.4 Hz, 9H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 201.68, 169.88, 169.08, 166.93, 160.45, 158.30, 158.25, 142.96, 142.92, 136.98, 136.43, 131.18, 131.13, 128.86, 128.69, 128.58, 128.47, 128.35, 126.80, 121.10, 117.23, 113.55, 109.13, 107.24, 91.05, 86.17, 71.94, 70.60, 69.74, 66.01, 65.82, 64.09, 35.90, 34.24, 26.05, 26.03, 24.29, 18.48, 18.23, 7.15, 7.10, 5.31, 5.15, 5.12, -1.26, -4.45, -4.81; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 1051.3986; found: 1051.3944 (ESI).




**4.5** **4.6**

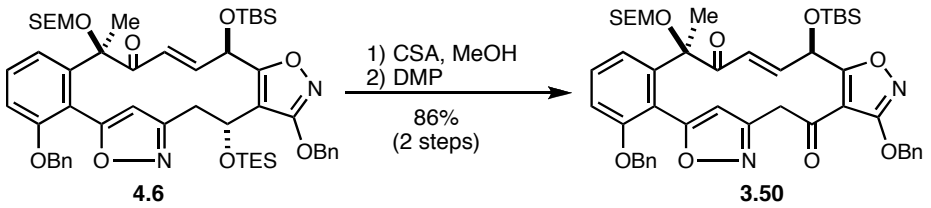
**Macrocyclic-enone (4.6).** To a solution of **4.5** (2.58 g, 2.45 mmol, 1.00 equiv.) in wet $CH_2Cl_2$ (12 mL, 0.20 M) at room temperature exposed to air, DMP (4.16 g, 9.80 mmol, 4.00 equiv.) was added in a single portion. The reaction was stirred for 3 h upon which time the cloudy mixture was poured into an Erlenmeyer flask containing pH 7 phosphate buffer (0.1 M buffer, 30 mL) and $Na_2S_2O_3$ (2 g). The reaction flask was washed three times with 10 mL portions of hexanes and this was poured into the vigorously stirring mixture within the Erlenmeyer flask. After 20 minutes of vigorous mixing, the reaction was extracted 3 times with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo* to yield crude aldehdye, which was immediately subjected to Reformatsky macrocyclization (*vide infra*).

A solution of intermediate aldehyde (2.45 mmol, crude from the reaction above) in degassed THF (61 mL, 0.040 M) at –78 °C under an atmosphere of argon was added to a solution of $SmI_2$ (98 mL of a 0.10 M solution in THF, 4.00 equiv.) at –78 °C via cannula directly into the solution over 10 minutes. THF (10 mL) was then used to wash the flask, and this too was added to the $SmI_2$ solution. The resulting dark blue solution was stirred at –78 °C for 30 minutes, upon which time air was bubbled through a glass pipet directly into the solution at –78 °C until the blue color disappeared and a yellow color persisted. A solution of sat. $NaHCO_3$ (20 mL) also containing $Na_2S_2O_3$ (1 g) was added and the reaction was allowed to warm to room temperature. The mixture was then ex-

tracted three times with $CH_2Cl_2$, the combined organic extracts were dried with $Na_2SO_4$, and concentrated *in vacuo*. The resulting residue was purified via MPLC (10% → 30% EtOAc and hexanes) affording the intermediate macrocyclic alcohol (1.64 g, 69%) as a mixture of secondary carbinol diastereomers that were dehydrated in the next step.

To a solution of the intermediate macrocyclic alcohol (1.64 mg, 1.69 mmol, 1.00 equiv.) in $CH_2Cl_2$ (24 mL, 0.070 M) at –45 °C under an atmosphere of nitrogen, the Martin sulfurane (24 mL of a 0.17 M solution in $CH_2Cl_2$, 2.4 equiv.) at room temperature was added along the side of the flask over 30 seconds. The reaction was allowed to warm to –10 °C over 1 hour, and held at this temperature for 3 h. The reaction was quenched via the addition of sat. $NaHCO_3$ (20 mL) and warmed to room temperature while stirring vigorously. The biphasic mixture was extracted three times with $CH_2Cl_2$ and the combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The resulting residue was purified via MPLC (5% → 35% EtOAc and hexanes) affording **4.6** (1.17 g, 73%) as a white foam and starting material (267 mg, 16%). Yield for the three steps: 47%. $\boldsymbol{R_f}$ = 0.29 (4:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –120 (*c* 0.95, $CHCl_3$); **IR** (neat) 2955, 2877, 1699, 1633, 1578, 1510, 1454, 1362, 1251, 1121, 1251, 1121, 1080, 1014, 745, 696; **$^1$H NMR** (500 MHz, $d_6$-DMSO) δ 7.59 – 7.47 (m, 3H), 7.44 – 7.34 (m, 3H), 7.34 – 7.16 (m, 8H), 7.03 (d, *J* = 15.3 Hz, 1H), 6.53 – 6.33 (m, 2H), 5.57 (s, 1H), 5.36 (s, 2H), 5.23 – 4.97 (m, 2H), 4.76 – 4.50 (m, 2H), 3.72 (d, *J* = 8.7 Hz, 1H), 3.51 – 3.32 (m, 2H), 2.95 (d, *J* = 13.3 Hz, 1H), 1.66 (s, 3H), 1.02 – 0.86 (m, 18H), 0.87 – 0.77 (m, 2H), 0.72 – 0.55 (m, 6H), 0.08 (d, *J* = 27.3 Hz, 6H), -0.02 (s, 9H); **$^{13}$C NMR** (126 MHz, $d_6$-DMSO) δ 199.58, 170.19, 166.64, 165.43, 158.17, 157.62, 144.50, 141.90, 136.69, 136.09, 130.85, 128.30, 128.26, 128.07, 127.59, 127.48, 126.72, 120.85, 120.20, 117.36, 113.72, 109.20, 108.20, 90.04,

84.14, 70.89, 69.48, 67.85, 65.02, 63.57, 33.69, 25.75, 22.83, 18.21, 17.53, 6.61, 4.67, -1.39, -5.08, -5.28; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 953.4618; found: 953.4574 (ESI).

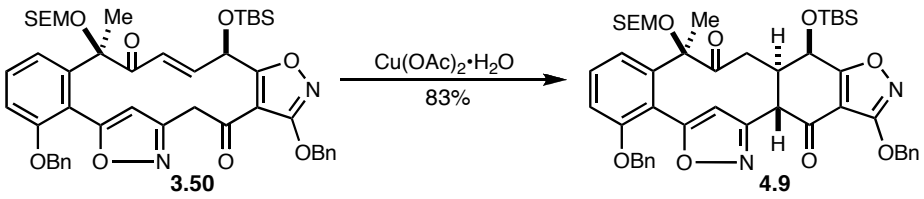



**4.6** **3.50**

**Elaborated macrocycle (3.50).** To a solution of **4.6** (1.17 g, 1.23 mmol, 1.00 equiv.) in methanol (12 mL, 0.10 M) and $CH_2Cl_2$ (3.0 mL, 0.41 M) at 0 °C under an atmosphere of nitrogen, CSA (29 mg, 0.12 mmol, 0.10 equiv.) was added in a single portion. The resulting solution was stirred for 1.5 h, upon which time the reaction was quenched with sat. $NaHCO_3$, warmed to room temperature, and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via MPLC (5% → 30% EtOAc and hexanes) affording the intermediate secondary carbinol (999 mg, 97%) as a colorless foam.

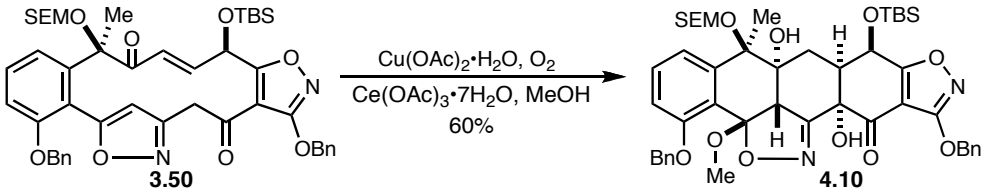
To a solution of the intermediate secondary carbinol (999 mg, 1.19 mmol, 1.00 equiv.) in wet $CH_2Cl_2$ (12 mL, 0.10 M) at room temperature exposed to air, DMP (2.02 g, 4.76 mmol, 4.00 equiv.) was added in a single portion. The reaction was stirred for 2 h, upon which time the reaction was poured into an Erlenmeyer flask containing sat. $NaHCO_3$ (20 mL) and $Na_2S_2O_3$ (2 g). The original reaction flask was washed liberally with hexanes and these washings were poured into the vigorously mixing solution. After 10

minutes, the mixture was poured into a separatory funnel, the organic layer was removed, and the remaining aqueous layer was extracted two times more with hexanes. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via MPLC (5% → 20% EtOAc and hexanes) affording **3.50** (882 mg, 89%) as a white foam. Yield for the two steps: 86%. $\boldsymbol{R_f}$ = 0.56 (4:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –75 (*c* 2.1, $CHCl_3$); **IR** (neat) 2952, 2930, 1686, 1617, 1591, 1506, 1452, 1438, 1251, 1120, 1082, 1055, 1011, 837, 749, 696, 870; **$^1$H NMR** (500 MHz, $d_6$-DMSO) δ 7.60 (d, *J* = 7.3 Hz, 2H), 7.52 (t, *J* = 8.1 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.40 (dd, *J* = 6.9, 1.7 Hz, 1H), 7.31 (dd, *J* = 7.9, 6.4 Hz, 2H), 7.29 – 7.19 (m, 5H), 6.84 – 6.39 (m, 2H), 6.10 – 5.84 (m, 1H), 5.61 – 5.31 (m, 2H), 5.11 (s, 2H), 4.65 – 4.31 (m, 2H), 3.83 (d, *J* = 13.3 Hz, 1H), 3.64 – 3.49 (m, 1H), 3.33 (s, 1H), 1.62 (s, 3H), 0.91 (s, 9H), 0.75 (ddd, *J* = 9.7, 6.5, 3.2 Hz, 2H), 0.09 (d, *J* = 12.5 Hz, 6H), -0.03 (s, 9H); **$^{13}$C NMR** (126 MHz, $d_6$-DMSO) δ 199.96, 188.85, 174.85, 168.08, 166.47, 157.53, 155.98, 142.66, 141.76, 136.63, 135.37, 131.23, 128.65, 128.58, 128.55, 128.50, 128.46, 128.42, 128.33, 128.28, 128.22, 128.16, 128.10, 128.01, 127.96, 127.76, 127.65, 127.57, 126.78, 126.68, 123.15, 121.07, 116.08, 113.57, 108.07, 89.83, 84.38, 72.01, 69.51, 67.51, 64.91, 25.45, 22.74, 17.84, 17.52, -1.38, -1.42, -1.45, -5.16, -5.35; **HRMS**: Exact mass calcd for [$(M+H^+)$]: 837.3597; found: 837.3556 (ESI).



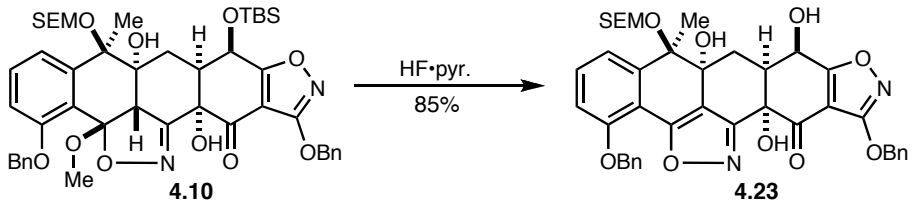

**Transannular Michael product 4.9.** To **3.50** (36 mg, 0.043 mmol, 1.0 equiv.) in degassed methanol (4.3 mL, 0.010 M) at room temperature under an argon atmosphere, $Cu(OAc)_2 \bullet H_2O$ (86 mg, 0.43 mmol, 10 equiv.) was added in a single portion. The reaction was immediately sealed, and allowed to stir at room temperature for 1.5 h. The blue/green solution was quenched with sat. $NaHCO_3$, diluted with water, and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (3:1 hexanes:EtOAc) affording **4.9** (30 mg, 83%) as a colorless oil. $\boldsymbol{R_f}$ = 0.24 (3:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –111 (*c* 1.5, $CHCl_3$); **IR** (neat) 2941, 2837, 1707, 1509, 1473, 1363, 1264, 1119, 1060, 998, 836, 751, 696; **$^1$H NMR** (600 MHz, *d*6-Acetone) δ 7.56 (ddt, *J* = 7.5, 1.3, 0.7 Hz, 2H), 7.51 (t, *J* = 8.2 Hz, 1H), 7.49 – 7.41 (m, 4H), 7.40 – 7.33 (m, 4H), 7.33 – 7.27 (m, 2H), 7.18 (s, 1H), 5.41 (d, *J* = 2.6 Hz, 2H), 5.34 – 5.21 (m, 2H), 5.06 (d, *J* = 2.8 Hz, 1H), 4.77 (d, *J* = 7.4 Hz, 1H), 4.67 (d, *J* = 7.4 Hz, 1H), 4.33 (d, *J* = 10.8 Hz, 1H), 3.98 (dd, *J* = 16.9, 10.9 Hz, 1H), 3.79 (td, *J* = 9.6, 6.3 Hz, 1H), 3.50 (td, *J* = 9.6, 6.5 Hz, 1H), 2.94 (tdd, *J* = 10.8, 2.8, 1.3 Hz, 1H), 2.25 (m, 1H), 1.69 (s, 3H), 0.97 (s, 9H), 0.86 (td, *J* = 9.7, 6.3 Hz, 2H), 0.34 (s, 3H), 0.18 (s, 3H), 0.01 (s, 9H); **$^{13}$C NMR** (126 MHz, *d*6-Acetone) δ 203.48, 186.20, 181.73, 171.04, 168.74, 160.92, 158.38, 145.73, 137.95, 136.69, 132.06, 129.48, 129.47, 129.42, 129.39, 128.81, 128.28, 123.07, 118.41, 114.54, 112.26, 107.43, 91.15, 85.80, 73.04, 71.30, 66.69, 66.38, 50.19, 49.64, 38.45,

26.32, 24.72, 19.02, 18.71, -1.00, -4.44; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 837.3597; found: 837.3534 (ESI).



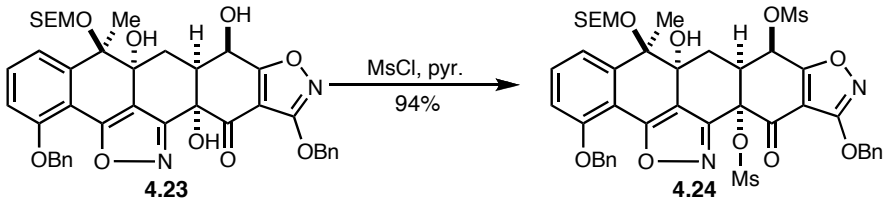

**Cascade product 4.10.** To **3.50** (390 mg, 0.466 mmol, 1.00 equiv.) at room temperature in methanol (7.8 mL, 0.060 M) exposed to air, $Cu(OAc)_2•H_2O$ (4.7 mg, 0.023 mmol, 0.050 equiv.) was added in a single portion, followed by $Ce(OAc)_3•H_2O$ (591 mg, 1.86 mmol, 4.00 equiv.) also in a single portion. The reaction was immediately fitted with a rubber septum, and $O_2$ from a balloon was bubbled through the solution for 5 minutes upon which time the needle was withdrawn from direct contact with the solution and the outlet needle was removed. The reaction was stirred under a balloon of $O_2$ for 44 h, upon which time the reaction was diluted with $CH_2Cl_2$ and filtered through celite. The resulting mixture was concentrated *in vacuo* and purified via MPLC (10% → 35% EtOAc and hexanes) affording **4.10** (239 mg, 60%) as a white foam. $\boldsymbol{R_f}$ = 0.51 (3:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –71 (*c* 0.75, $CHCl_3$); **IR** (neat) 3300, 2951, 2858, 1702, 1613, 1580, 1514, 1363, 1251, 1128, 1087, 1013, 859, 838, 744, 696; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.67 – 7.56 (m, 2H), 7.32 – 7.20 (m, 4H), 7.12 – 7.07 (m, 1H), 7.07 – 6.99 (m, 4H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.62 (dd, *J* = 8.4, 1.0 Hz, 1H), 5.61 (d, *J* = 6.1 Hz, 1H), 5.18 – 5.00 (m, 2H), 4.98 – 4.78 (m, 2H), 4.48 (d, *J* = 7.4 Hz, 1H), 4.30 (d, *J* = 7.3 Hz, 1H), 4.28 – 4.13 (m, 2H), 3.79 (s, 3H), 3.64 (ddd, *J* = 13.1, 6.2, 4.1 Hz, 1H), 3.44 (td, *J* = 9.9, 6.0 Hz, 1H),

3.09 (td, *J* = 9.9, 6.2 Hz, 1H), 2.66 (dd, *J* = 13.9, 4.1 Hz, 1H), 1.95 (td, *J* = 13.6, 2.6 Hz, 1H), 1.73 (s, 3H), 0.95 (s, 9H), 0.85 – 0.61 (m, 2H), 0.11 (s, 3H), 0.02 (s, 3H), -0.10 (s, 9H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 186.29, 180.64, 168.68, 159.79, 159.38, 137.86, 137.02, 135.57, 130.25, 128.73, 128.65, 128.55, 128.35, 127.72, 127.07, 123.15, 120.82, 114.98, 107.45, 104.35, 90.70, 80.74, 78.47, 76.84, 72.47, 70.64, 65.21, 64.82, 57.11, 51.56, 50.89, 28.83, 25.82, 18.42, 18.12, 17.70, -1.35, -5.02, -5.15; **HRMS**: Exact mass calcd for [(M-MeOH+H$^+$)]: 853.3546; found: 853.3593 (ESI).




**Secondary carbinol 4.23.** To a solution of 5:2:3 THF:pyr.:HF•pyr. (2.1 mL, 25 ml solution/mmol sm) at room temperature exposed to air, **4.10** (72 mg, 0.084 mmol, 1.0 equiv.) in THF (2.1 mL, 0.040 M) was added rapidly. The plastic tube was sealed and heated to 35 °C for 23 h, upon which time the reaction was quenched with sat. $NaHCO_3$ (careful, gas evolution) and extracted three times with EtOAc. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (3:2 hexanes:EtOAc) affording **4.23** (53 mg, 85%) as a colorless oil. $R_f$ = 0.32 (2:1 EtOAc:hexanes); $[\alpha]_D$ = –110 (*c* 0.95, $CHCl_3$); **IR** (neat) 3379, 2950, 2893, 1707, 1613, 1573, 1513, 1450, 1370, 1247, 1069, 1016, 837, 740, 698; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.43 (d, *J* = 7.5 Hz, 2H), 7.36 – 7.23 (m, 4H), 7.16 – 6.99 (m, 5H), 6.90 (t, *J* = 8.1 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 5.93 – 5.48 (m, 2H), 5.16 (d, *J* =

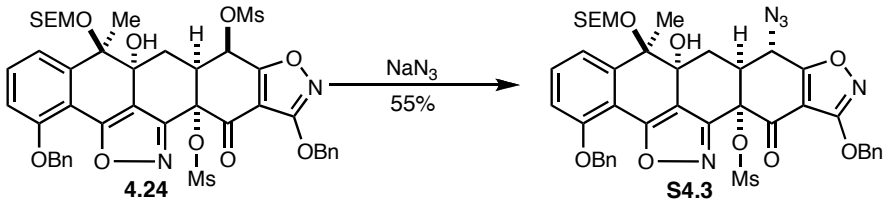
11.7 Hz, 1H), 4.95 (d, *J* = 11.8 Hz, 1H), 4.78 (q, *J* = 12.4 Hz, 2H), 4.06 (m, 2H), 3.89 (s, 1H), 3.59 (s, 1H), 3.17 (q, *J* = 8.6 Hz, 1H), 2.93 (q, *J* = 8.5 Hz, 1H), 2.78 (d, *J* = 13.6 Hz, 1H), 2.26 (t, *J* = 13.4 Hz, 1H), 1.70 (s, 3H), 0.63 (t, *J* = 8.1 Hz, 2H), -0.06 (s, 9H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 185.11, 180.85, 168.65, 163.84, 159.15, 155.17, 141.30, 136.83, 135.64, 130.92, 128.94, 128.66, 128.54, 128.51, 127.41, 122.46, 117.78, 114.96, 114.41, 104.26, 89.82, 81.02, 72.45, 70.98, 70.13, 65.09, 63.75, 47.83, 18.02, 16.43, -1.21; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 739.2681; found: 739.2641 (ESI).




**4.23** **4.24**

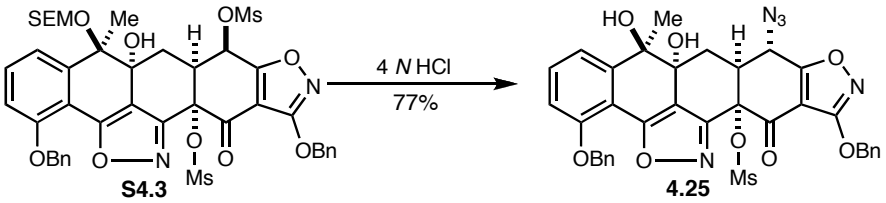
**Bis-mesylate 4.24.** To a solution of **4.23** (23 mg, 0.031 mmol, 1.0 equiv.) in $CH_2Cl_2$ at room temperature under an atmosphere of nitrogen, pyridine (88 μL, 1.1 mmol, 35 equiv.) was added rapidly, followed by MsCl (60 μL, 0.78 mmol, 25 equiv.). The flask was immediately sealed and heated to 35 °C for 5.5 h, upon which time the reaction was quenched with sat. $NaHCO_3$ and extracted three times with $CH_2Cl_2$. The combined organic extracts were then dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (3:2 hexanes:EtOAc) affording **4.24** (25 mg, 94%) as a colorless oil. $R_f$ = 0.52 (1:1 hexanes:EtOAc); $[\alpha]_D$ = –65 (*c* 0.075, $CHCl_3$); **IR** (neat) 2922, 2854, 1723, 1653, 1521, 1478, 1368, 1182, 1007, 944, 836; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.20 (q, *J* = 7.8, 7.3 Hz, 3H), 7.12 – 6.95 (m, 4H), 6.88 (m, 3H), 6.60 (d, *J* = 8.1 Hz, 1H), 5.02 (d, *J* = 12.2 Hz, 1H), 4.95 –

4.77 (m, 5H), 4.09 – 3.93 (m, 2H), 3.11 (q, *J* = 8.7 Hz, 1H), 2.95 (q, *J* = 8.6 Hz, 1H), 2.68 – 2.56 (m, 4H), 2.36 (d, *J* = 16.8 Hz, 4H), 1.45 (s, 3H), 0.63 (t, *J* = 8.2 Hz, 2H), -0.04 (s, 9H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 176.16, 174.55, 168.48, 164.51, 155.48, 154.89, 140.21, 136.83, 135.23, 131.20, 128.96, 128.69, 128.66, 127.21, 122.24, 118.08, 114.84, 114.07, 106.39, 89.76, 87.45, 80.59, 72.66, 70.78, 70.38, 69.17, 65.11, 46.25, 40.56, 38.04, 29.24, 18.09, 16.24, -1.26; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 895.2232; found: 895.2190 (ESI).



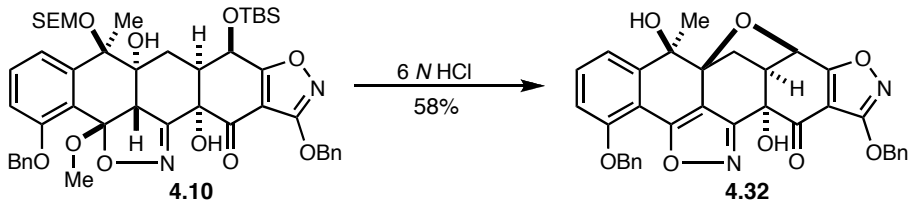

**Azide S4.3.** To a solution of **4.24** (24 mg, 0.028 mmol, 1.0 equiv.) in 2:1 DMF:water (3.0 mL, 0.010 M) at room temperature exposed to air, $NaN_3$ (55 mg, 0.84 mmol, 30 equiv.) was added in a single portion. The reaction was stirred at room temperature for 18 h, upon which time it was diluted with water and extracted three times with EtOAc. The combined organic extracts were washed with brine, dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via HPLC (5% *i*-PrOH and hexanes) affording **S4.3** (13 mg, 55%) as a colorless oil. $R_f$ = 0.42 (1:1 hexanes:EtOAc); $[\alpha]_D$ = +20 (*c* 0.55, $CHCl_3$); **IR** (neat) 3504, 2951, 2110, 1717, 1573, 1515, 1370, 1248, 1178, 1018, 926, 859, 816, 696; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.58 – 7.48 (m, 2H), 7.40 – 7.32 (m, 2H), 7.26 – 7.09 (m, 3H), 7.10 – 7.02 (m, 2H), 7.01 – 6.92 (m, 3H), 6.64 (d, *J* = 8.2 Hz, 1H), 5.35 (d, *J* = 4.5 Hz, 1H), 5.14 (m, 2H), 4.87 (m, 2H), 4.20 (m, 2H), 3.57 – 3.37 (m, 1H),

3.30 – 3.02 (m, 3H), 2.28 (s, 3H), 2.22 (dd, *J* = 13.7, 2.0 Hz, 1H), 1.74 (s, 3H), 1.41 (s, 1H), 0.76 (ddd, *J* = 9.5, 6.5, 4.3 Hz, 2H), -0.02 (s, 9H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 179.92, 173.44, 168.65, 164.42, 155.52, 155.06, 140.56, 136.69, 135.29, 131.12, 129.00, 128.86, 128.82, 128.60, 128.56, 127.01, 122.21, 116.97, 114.90, 114.13, 107.74, 90.04, 80.71, 72.78, 70.77, 69.62, 69.09, 65.31, 65.29, 41.85, 38.29, 29.84, 18.18, 16.21, -1.25; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 842.2522; found: 842.2551 (ESI).




**Deprotected Azide 4.25.** To a solution of **S4.3** (11 mg, 0.0131 mmol, 1.0 equiv.) in THF (1.5 mL, 0.0087 M) at room temperature exposed to air, 4 *N* HCl (1.5 mL, 0.0087 M) was added rapidly. The reaction was stirred at room temperature for 2.5 h, upon which time it was quenched with sat. $NaHCO_3$ and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via flash chromatography on silica gel (1:1 hexanes:EtOAc) affording **4.25** (7.1 mg, 77%) as a white solid. $\boldsymbol{R_f}$ = 0.21 (1:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = +48 (*c* 0.26, $CHCl_3$); **IR** (neat) 3508, 3027, 2937, 2853, 2110, 1714, 1650, 1572, 1515, 1476, 1367, 1270, 1227, 1177, 1086, 1028, 959, 924; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.56 – 7.47 (m, 2H), 7.39 – 7.31 (m, 2H), 7.23 – 7.10 (m, 4H), 7.10 – 7.02 (m, 2H), 6.93 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.59 (d, *J* = 8.3 Hz, 1H), 5.35 (d, *J* = 4.0 Hz, 1H), 5.21 – 5.05 (m, 2H), 4.96 – 4.79 (m, 2H), 3.13 – 2.95 (m, 2H), 2.23 (s, 3H), 2.15 (d, 1H), 1.52

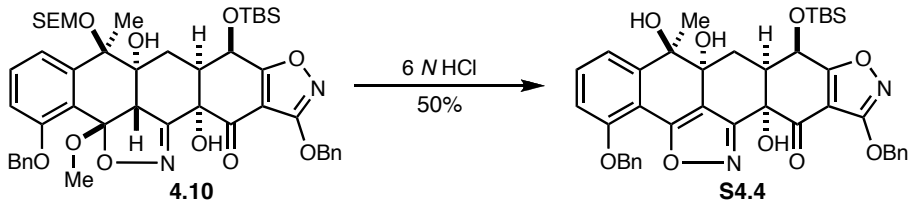
(s, 4H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 179.93, 173.53, 168.62, 164.04, 155.42, 155.33, 143.91, 136.69, 135.29, 131.89, 129.03, 128.85, 128.83, 128.61, 128.57, 127.06, 119.88, 116.07, 113.97, 113.75, 107.67, 75.48, 72.78, 70.72, 69.81, 68.51, 65.20, 41.61, 38.13, 29.47, 19.23; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 712.1708; found: 712.1717 (ESI).




**4.10** **4.32**

**Polycycle 4.32.** To a solution of **4.10** (60 mg, 0.070 mmol, 1.0 equiv.) in THF (4.7 mL, 0.015 M) at room temperature exposed to air, 6 *N* HCl (2.3 mL, 0.030 M) was added rapidly. The reaction was then sealed and heated to 35 °C for 7 h. The resulting slightly yellow solution was cooled to room temperature quenched with sat. $NaHCO_3$ (caution, gas evolution) and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via MPLC (30% → 70% EtOAc and hexanes) affording **4.10** (24 mg, 58%) as a white solid. $R_f$ = 0.33 (1:1 hexanes:EtOAc); $[\alpha]_D$ = +217 (*c* 1.0, CH2Cl2); **IR** (neat) 3417, 2925, 1714, 1680, 1514, 1454, 1360, 1286, 1264, 1233, 1080, 1013, 873, 736; **$^1$H NMR** (600 MHz, Benzene-d6) δ 7.53 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.37 – 7.24 (m, 2H), 7.24 – 7.16 (m, 2H), 7.12 – 6.94 (m, 7H), 6.36 (dd, *J* = 8.4, 0.9 Hz, 1H), 4.99 (d, *J* = 12.0 Hz, 1H), 4.83 (s, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.63 (d, *J* = 12.3 Hz, 1H), 4.54 (d, *J* = 12.4 Hz, 1H), 4.30 (d, *J* = 5.9 Hz, 1H), 3.09 – 2.97 (m, 1H), 2.79 – 2.63 (m, 1H), 2.30 (d, *J* = 11.9 Hz, 1H), 1.93 (dd, *J* = 12.0, 4.9 Hz, 1H), 1.11 (s, 3H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ 186.95,

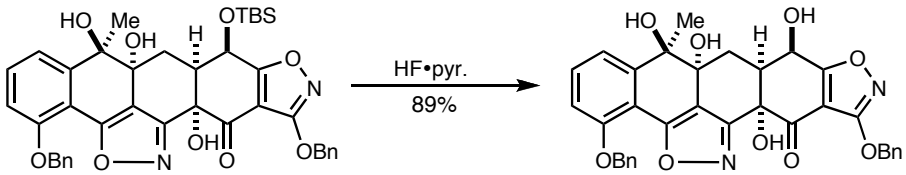
176.18, 167.54, 162.71, 159.47, 154.80, 148.13, 136.83, 135.36, 132.22, 128.74, 128.69, 128.64, 128.57, 126.88, 119.18, 115.28, 112.64, 112.43, 105.96, 81.96, 74.48, 73.50, 72.59, 70.42, 68.64, 49.28, 32.52, 28.91; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 613.1581; found: 613.1604 (ESI).




**4.10** **S4.4**

**Triol S4.4.** To a solution of **4.10** (239 mg, 0.279 mmol, 1.00 equiv.) in THF (8.0 mL, 0.030 M) at room temperature exposed to air, 6 *N* HCl (4.0 mL, 0.060 M) was added rapidly. The reaction was then sealed stirred at room temperature for 6 h. The resulting slightly yellow solution was quenched with sat. $NaHCO_3$ (caution, gas evolution) and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The crude residue was purified via MPLC (15% → 40% EtOAc and hexanes) affording **S4.4** (100 mg, 50%) as a white solid. $\boldsymbol{R_f}$ = 0.40 (2:1 hexanes:EtOAc); $\boldsymbol{[\alpha]_D}$ = –140 (*c* 0.85, $CHCl_3$); **IR** (neat) 3423, 2929, 2857, 1707, 1513, 1481, 1452, 1365, 1263, 1079, 1045, 840, 784, 736; **$^1$H NMR** (500 MHz, $C_6D_6$) δ 7.59 – 7.48 (m, 2H), 7.34 – 7.27 (m, 2H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.13 – 7.02 (m, 3H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 7.0 Hz, 2H), 6.56 (dd, *J* = 6.8, 2.5 Hz, 1H), 5.82 (d, *J* = 5.8 Hz, 1H), 5.08 (q, 1H), 4.95 – 4.83 (m, 3H), 3.48 (ddd, *J* = 13.2, 5.9, 2.2 Hz, 1H), 2.54 (dd, *J* = 13.9, 2.3 Hz, 1H), 2.07 (t, *J* = 13.5 Hz, 1H), 1.49 (s, 3H), 1.29 (s, 1H), 1.25 – 1.19 (m, 1H), 1.01 (s, 9H), 0.19 (d, *J* = 19.1 Hz, 6H); **$^{13}$C NMR** (126 MHz, $C_6D_6$) δ

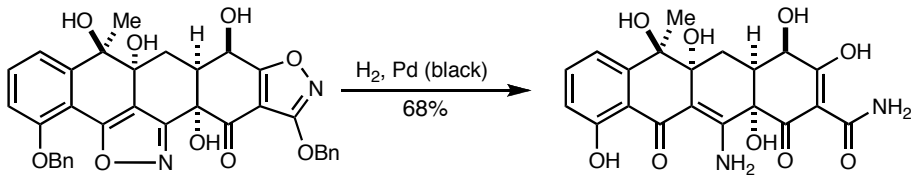
184.46, 180.12, 168.84, 163.25, 159.03, 155.18, 144.53, 137.11, 135.80, 131.74, 128.99, 128.63, 128.48, 128.46, 127.10, 120.09, 117.12, 113.84, 113.39, 104.33, 103.30, 78.38, 75.76, 72.28, 70.51, 69.72, 64.65, 48.21, 36.84, 26.82, 25.94, 25.03, 18.67, 18.55, -4.85, -4.90; **HRMS**: Exact mass calcd for [(M+H$^+$)]: 723.2732; found: 723.2749 (ESI).




**S4.4** **4.37**

**Tetraol 4.37.** To a solution of 5:2:6 THF:pyr.:HF•pyr. (3.5 mL, 25 ml solution/mmol sm) at room temperature exposed to air, **S4.4** (100 mg, 0.138 mmol, 1.00 equiv.) in THF (4.6 mL, 0.030 M) was added rapidly. The plastic tube was sealed and heated to 30 °C for 14 h, upon which time the reaction was quenched with sat. $NaHCO_3$ (careful, gas evolution) and extracted three times with $CH_2Cl_2$. The combined organic extracts were dried with $Na_2SO_4$ and concentrated *in vacuo*. The resulting residue was purified via purified via MPLC (40% → 80% EtOAc and hexanes) affording **4.37** (75 mg, 89%) as a white solid. $R_f$ = 0.53 (2:1 EtOAc:hexanes); $[\alpha]_D$ = –48 (*c* 0.80, $CH_2Cl_2$); **IR** (neat) 3390, 1698, 1652, 1614, 1574, 1515, 1486, 1455, 1372, 1270, 1077, 1042, 799, 736, 697; **$^1$H NMR** (600 MHz, CD3CN) δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.52 (m, 2H), 7.52 – 7.40 (m, 5H), 7.34 (d, *J* = 7.9 Hz, 0H), 7.24 (d, *J* = 8.5 Hz, 2H), 5.75 (d, *J* = 5.8 Hz, 1H), 5.46 – 5.27 (m, 4H), 5.00 (s, 1H), 4.53 (s, 1H), 3.47 (ddd, *J* = 13.0, 5.8, 2.3 Hz, 1H), 3.40 (s, 1H), 3.17 (s, 1H), 2.33 (dd, *J* = 13.9, 2.3 Hz, 1H), 1.83 (t, *J* = 13.5 Hz, 1H), 1.66 (s, 3H); **$^{13}$C NMR** (126 MHz, $CD_3CN$) δ 185.12, 181.53, 169.24, 164.12, 159.44, 155.73,

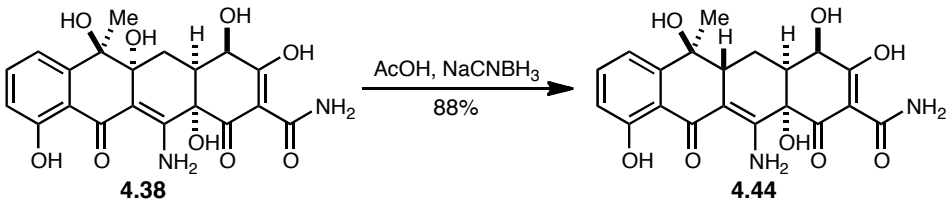
145.66, 138.03, 136.40, 132.61, 129.64, 129.57, 129.54, 129.51, 128.86, 128.30, 120.73, 117.75, 114.53, 114.27, 104.35, 78.87, 76.36, 73.28, 71.21, 70.14, 63.39, 48.39, 27.29, 19.38; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 631.1687; found: 631.1675 (ESI).




4.37 4.38

**(4*R*,4a*S*,5a*R*,6*R*,12a*S*)-12-amino-3,4,5a,6,10,12a-hexahydroxy-6-methyl-1,11-dioxo-1,4,4a,5,5a,6,11,12a-octahydrotetracene-2-carboxamide (4.38).** To a solution of **4.38** (25 mg, 0.041 mmol, 1.0 equiv.) in degassed 4:1 dioxane:water (4.0 mL, 0.010 M) at room temperature, Pd black (12 mg, 0.11 mmol, 2.8 equiv.) was added. A balloon of $H_2$ was then fitted to the flask with a needle, and $H_2$ was bubbled through the solution for 5 minutes. The resulting slightly yellow suspension was stirred for 24 h, upon which time Ar was bubbled through the solution for 5 minutes to purge the remaining hydrogen. The reaction was then filtered while washing with methanol. The filtrate was then concentrated *in vacuo*. The resulting residue was purified via reverse phase MPLC (0% → 100% $CHC_3CN$ and water) affording **4.38** (12 mg, 68%) as a slightly yellow solid. $[\alpha]_D$ = +371.9 (*c* 0.36, THF); **IR** (neat) 3410, 2979, 1607, 1461, 1352, 1262, 1240, 1037, 995; **$^1$H NMR** (600 MHz, $CD_3OD$) δ 7.41 (t, *J* = 8.0 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.76 (dd, *J* = 8.3, 1.1 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 3.11 – 2.96 (m, 1H), 2.47 (dd, *J* = 11.3, 5.0 Hz, 1H), 2.38 (d, *J* = 11.4 Hz, 1H), 1.39 (s, 3H); **$^{13}$C NMR** (126 MHz, $CD_3OD$) δ 195.15, 193.00, 188.98, 174.23, 162.76, 162.26, 149.87, 135.61, 116.91, 116.33,

115.27, 104.12, 98.40, 87.19, 76.91, 76.00, 72.03, 43.31, 32.51, 30.17; **HRMS**: Exact mass calcd for [(M–$H_2O$+$H^+$)]: 415.1136; found: 415.1154 (ESI).




**4.38** **4.44**

**C12-amino-4-hydroxy-tetracycline (4.44).** To a solution of **4.38** (6.5 mg, 0.015 mmol, 1.0 equiv.) in $CH_3CN$ (2.0 mL, 0.0075 M) at room temperature exposed to air, $NaCNBH_3$ (3.0 mg, 0.048 mmol, 3.2 equiv.) was added, followed by AcOH (10 $\mu$L, 0.17 mmol, 12 equiv.). The resulting yellow solution was sealed and stirred at 30 °C for 14 h, during which time the product slowly precipitated from the reaction mixture. The resulting suspension was diluted with methanol and concentrated *in vacuo*. The crude residue was purified via reverse phase MPLC (10% → 60% $CH_3CN$ and water) affording **4.44** (5.5 mg, 88%) as a yellow solid. $[\alpha]_D$ = –130 (*c* 0.28, MeOH); **IR** (neat) 3366, 2918, 2864, 2371, 2255, 1606, 1573, 1460, 1362, 1255, 1120, 1025, 872, 824; **$^1$H NMR** (600 MHz, $d_6$-DMSO) δ 13.53 (s, 1H), 10.38 (s, 1H), 9.47 – 8.79 (m, 2H), 7.72 (s, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.18 – 6.96 (m, 1H), 6.87 – 6.57 (m, 2H), 5.79 (s, 1H), 5.07 (s, 1H), 4.72 (s, 1H), 2.76 (dd, *J* = 9.5, 2.4 Hz, 1H), 2.57 (dt, *J* = 12.9, 5.3 Hz, 1H), 2.47 (d, *J* = 16.2 Hz, 1H), 1.26 (ddd, *J* = 15.0, 12.5, 9.8 Hz, 1H), 1.11 (s, 3H); **$^{13}$C NMR** (126 MHz, $CD_3OD$) δ 197.55, 191.96, 190.80, 175.21, 164.55, 162.56, 152.09, 135.19, 116.97, 116.68, 114.88, 99.53, 97.23, 77.22, 75.36, 70.94, 43.64, 41.18, 24.19, 19.31; **HRMS**: Exact mass calcd for [(M+$Na^+$)]: 439.1112; found: 439.1133 (ESI).

## B. Computational Methods

*Molecular Mechanics*. All molecular mechanics calculations were performed using Spartan 2008, v. 1.1.2 (Wavefunction, Inc., Irvine, CA, USA), using the molecular mechanics MM2 force field. To generate an initial subset of reasonable conformers, a conformer dis-

tribution calculation was performed, and the 100 structures of lowest energy were documented. This procedure was performed at least three times with three different starting conformers, generating a total of 300 conformers for each macrocyclic enolate. A subset of these conformers was then further optimized via DFT.

*Density Functional Theory.* All DFT calculations were performed using Gaussian 09 (Revision A.02)[172] on the Odyssey Cluster at Harvard University. Each starting structure, already a local minimum with respect to the MM PES, was re-optimized with the B3LYP hybrid functional[173] with the 6-31G* (for H, C, O, and N) and MDF10 (for Cu) basis sets. Structures marked as transition states were found to have exactly one negative frequency. The SMD implicit solvation model[174] was used in all cases with methanol as the specified solvent.

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[172] Gaussian 09, Revision A.02: Frisch, M. J.; Trucks. G. W.; Schlegel, H. B.; Scuseria G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann. R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian Inc., Wallingford, CT, **2009**.

[173] (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. (b) Stephens, P. J.; Devlin, F. J.; Chablowski, C. F.; Frisch, M. J. *J. Chem. Phys.* **1994**, *98*, 11623-11627.

[174] Marenich, A. V.; Cramer. C. J.; Truhlar, D. G. *J. Phys. Chem. B.* **2009**, *113*, 6378-6396.

# *Chapter 5*

## Analysis of the Peripheral Attack Model[175]

### I. Introduction

Conformational analysis is an indispensable tool when attempting to assess the reactivity of organic molecules.[176] The coupling of both conformational analysis and reactivity was first demonstrated in the context cyclic alkanes in pioneering work conducted by Barton.[177] In those studies, the primary focus was to understand the affect of substituent positioning on reactivity, mainly within cyclohexane or fixed-ring steroidal systems. In the late 1970's and early 1980's, Still and co-workers began to look at medium rings (8-12 membered rings) as molecular entities with defined conformations, initially articulating this point via racemic synthesis of the sex excitant pheromone periplanone.[178] Within this disclosure the potential generality of the approach was discussed by means of the following statement:

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[175] All material within this chapter was generated in collaboration with Dr. Eugene Kwan. Both Dr. Kwan and I contributed equally to this work.

[176] For an excellent review of conformational analysis concepts, see: *Stereochemistry of Organic Compounds;* Eliel, E. L.; Wilen, S. H. John Wiley & Sons, Inc.: New York, 1994.

[177] (a) Barton, D. H. R. *Experentia*, **1950**, *6*, 316-320. (b) Barton, D. H. R.; *Science*. **1970**, *169*, 539-544.

> *"This principle of peripheral attack appears to be a general strategy for stereochemical control in the synthesis and modification of germacranes and related medium-ring compounds. It does, however, require knowledge of the conformation of the starting olefin."*[178]

"Peripheral attack", as used above, refers to the propensity for reagents (nucleophiles or electrophiles) to approach macrocyclic π-bonds from the exterior rather than interior. Three types of π-bond orientations with respect to the macrocycle exist (Figure 5.1), with the 1,1'-extra-annular case (**5.2**) applicable for both an exocyclic olefin and a carbonyl function. Thus, with the discovery that a medium ring system can be used to ones advantage in synthesis as demonstrated by Still and co-workers, many new opportunities were created for organic chemists.

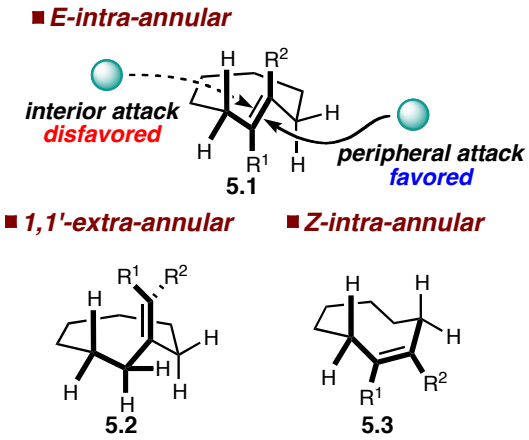


**Figure 5.1** Peripheral attack as it applies to different π-bond orientations. Example **5.2** is also relevant for carbonyl additions. The green sphere represents a generic nucleophile, however electrophiles are valid as well.

[178] Still, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 2493-2495.

The concept of peripheral attack is a component of the larger 'peripheral attack model'.[179] This model represents a ground state approach to selectivity prediction within the context of medium and large rings (> 7 membered), and is only relevant for intermolecular reactions.[180] More specifically, the ground state conformational bias of a given substrate may be directly translated to a stereochemical prediction based upon the difference in energy between the favored conformer and the lowest energy conformer leading to the opposite diastereochemical outcome ($E_{rel}$). Implicit within this analysis is that all other factors such as reaction type, nature of the reagent, and the development of any stereoelectronic or electrostatic interactions in the transition state are ignored. In essence, the model assumes that the π-facial bias from a given substrate conformation is significantly large such that all other interactions are negligible.

While Still did not invoke the Curtin-Hammett principle[133] in his discussion, the peripheral attack model also assumes a specific Curtin-Hammett condition (Figure 5.2) where the activation energies of the reactions from each ground state conformer (**GS-1**, **GS-2**) are similar ($\Delta G_1^{\ddagger} \sim \Delta G_2^{\ddagger}$ or $\Delta G^0 \sim \Delta\Delta G^{\ddagger}$). This places restrictions on both the types of reactions and structure of substrate that can be studied. Since reactions that proceed with a very low transition state barrier may compete with conformational mobility, and conformationally immobile systems may have barriers of interconversion that compete with reaction, the model needs to be applied judiciously.

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[179] Still, W. C.; Galynker, I. *Tetrahedron*. **1981**, *37*, 3981-3996.

[180] The model is only relevant for intermolecular reactions since intramolecular reactions rely upon attack from the interior of the ring.

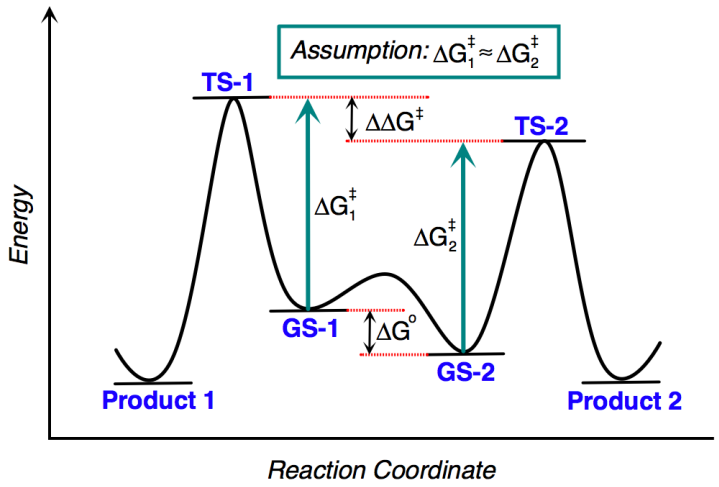


**Figure 5.2** The Curtin-Hammett system and ground state assumption implicit to the peripheral attack model.[133, 181]

Following the periplanone synthesis in 1979, perhaps the only remaining obstacle between this initially proposed model and widespread adoption was the development of a reliable method of semi-quantitative conformational prediction. This obstacle was overcome in 1981 when Still and co-workers further delineated the concept of peripheral attack within 8-12 membered ring systems by incorporating computations into the study of substrate conformational profiles.[179] In contrast to the periplanone synthesis, this work primarily sought to correlate the computed conformational profile of a given ring with the diastereoselectivity achieved from a given reaction using the ring as substrate. Importantly, this work achieved a "semi-quantitative prediction of product distributions in every case", and ultimately bridged the gap between conformational analysis and stereoselective synthesis by demonstrating the utility of computational chemistry within the con-

[181] It is assumed that $\Delta G^0 << \Delta G_1^{\ddagger}$ and $\Delta G^0 << \Delta G_2^{\ddagger}$, where **GS-1** and **GS-2** represent the two lowest energy conformers that lead to the two possible diastereomeric products of the reaction. Alternatively, if

text of macrocycles. Now the peripheral attack model could be applied to macrocyclic systems in a straightforward manner, effectively beginning an era of intermolecular macrocyclic stereocontrol.

## II. The Peripheral Attack Model in Modern Organic Synthesis

Since the initial study of macrocyclic conformation and reactivity, organic chemists have used macrocycles as stereocontrol elements widely.[182] Alarmingly, there are a significant number of instances where the peripheral attack model is used outside the context of the 10-12 membered rings in which it was initially established (select examples can be found in Figure 5.3). At times, literature disclosures describe the successful utilization of conformational analysis, yet one wonders if examples tend to go unreported in the cases of macrocyclic stereocontrol that defy prediction. Further, the utility and accuracy of the

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conformational interconversion is slow relative to reaction, then the ground state bias can still be recovered in the observed selectivity as long as the system is allowed to come to equilibrium before reaction.

[182] (a) Ref. [179]. (b) Kim, H.; Lee, H.; Kim, J.; Kim, S.; Kim, D. *J. Am. Chem. Soc.*, **2006**, *128*, 15851-15855. (c) Wang, B.; Ramirez, A. P. Slade, J. J.; Morken, J. P. *J. Am. Chem. Soc.* **2010**, *132*, 16380-16382. (d) Ref. [178]. (e) Ushakov, D. B.; Navickas, V.; Ströbele, M.; Maichle-Mössmer, C.; Sasse, F.; Maier, M. E. *Org. Lett.* **2011**, *13*, 2090-2093. (f) Vedejs, E.; Duncan, S. M. *J. Org. Chem.* **2000**, *65*, 6073-6081. (g) Still, W. C.; Macpherson, L. J.; Harada, T.; Callahan, J. F. *Tetrahedron*. **1984**, *40*, 2275-2281. (h) Tu, W.; Floreancig, P. E. *Angew. Chem. Int. Ed.* **2009**, *48*, 4567-4571. (i) Evans, D. A.; Ratz, A. M.; Huff, B. E.; Shepard, G. S. *J. Am. Chem. Soc.*, **1995**, *117*, 3448-3467. (j) Nicolaou, K. C.; Adsool, V. A.; Hale, C. R. H. *Angew. Chem. Int. Ed.*, **2011**, *50*, 5149-5152. (k) Urle, S. B.; Blume, T.; Mengel, A.; Parchmann, C.; Skuballa, W.; Bäsler, S. B.; Schäfer, M.; Sülzle, D.; Wrona-Metzinger, H.-P. *Angew. Chem. Int. Ed.* **2003**, *42*, 3961-3964. (l) Xu, Z.; Johannes, C. W.; Houri, A. F.; La, D. S.; Cogan, D. A.; Hofilena, G. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **1997**, *119*, 10302-10316. (m) Llácer, E.; Urpí, F.; Vilarrasa, J. *Org. Lett.* **2009**, *11*, 3198-3201. (n) Hu, T.; Takenaka, N.; Panek, J. S. *J. Am. Chem. Soc.* **2002**, *124*, 12806-12815. (o) Paterson, I.; Norcross, R. D.; Ward, R. A.; Romea, P. Lister, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 11287-11314. (p) Li, G.; Yang, X.; Zhai, H. *J. Org. Chem.* **2009**, *74*, 1356-1359. (q) Mulzer, J.; Kristein, H. M.; Buschmann, J.; Lehmann, C.; Luger, P. *J. Am. Chem. Soc.* **1991**, *113*, 910-923. (r) Stachel, S. J.; Danishefsky, S. J.; *Tet. Lett.* **2001**, *42*, 6785-6787. (s) Still, W. C.; Novack, V. J. *J. Am. Chem. Soc.* **1984**, *106*, 1148-1149. (t) Qibin, S.; Beeler, A. B.; Lobkovsky, E.; Porco Jr., J. A.; Panek, J. S. *Org. Lett.* **2003**, *5*, 2149-2152. (u) Layton, M. E.; Morales, C. A.; Shair, M. D. *J. Am. Chem. Soc.* **2002**, *124*, 773-775. (v) Kende, A. S.; Liu, K.; Kaldor, I.; Dorey, G.; Koch, K. *J. Am. Chem. Soc.* **1995**, *117*, 8258-8270. (w) Nicolaou, K. C.; Jiang, X.; Lindsay-Scott, P. J.; Corbu, A.; Yamashiro, S.; Bacconi, A.; Fowler, V. M. *Angew. Chem. Int. Ed.*

peripheral attack model itself has not been re-evaluated since the initial disclosure by Still and co-workers despite widespread adoption. Unfortunately, simple data mining of relevant literature examples is not possible due to either the lack of disclosure or lack of consistency within the computational details of conformational analysis. For these reasons, we believe that the peripheral attack concept should be uniformly re-evaluated in order to compare the predictions of conformational analysis to experimental observations. In doing so, this will enable both the systematization of the analysis for potential future use and an unbiased assessment of its utility and accuracy. Over thirty years ago the peripheral attack hypothesis was proposed; it is now our intent to identify whether the field of organic synthesis should continue to embrace or leave behind this longstanding model.

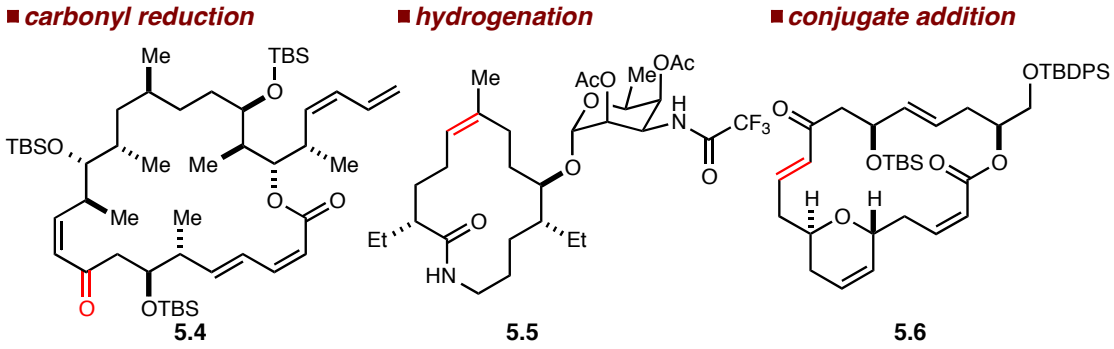


**Figure 5.3** Select literature examples that demonstrate the use of the peripheral attack model in the context of large macrocycles (>12 membered rings).[183]

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**2011**, *123*, 1171-1176. (x) Paterson, I.; Britton, R.; Delgado, O.; Meyer, A.; Poullennec, K. G. *Angew. Chem. Int. Ed.* **2004**, *116*, 4729-4733.

[183] Left example: ref. [182(x)]; middle example: ref. [182(l)]; right example: Patterson, I.; Savi, C. D.; Tudge, M. *Org. Lett.* **2001**, *3*, 213-216.

**III. Development of a Systematic Method for Stereochemical Prediction**

Two types of computational procedures were examined for implementing the peripheral attack model (Scheme 5.17): one involving only molecular mechanics ("MM") and one involving both molecular mechanics and DFT ("MM-DFT"). Both methods commenced with a relatively fast Monte Carlo conformational search for a given macrocycle bearing a reactive π-bond using molecular mechanics. With the MM method, the resulting geometries and energies were examined directly. With the MM-DFT method, the MM structures were further optimized in a slower process to local minima with DFT. In many cases, the initial set of MM conformers was very large; therefore, relevant conformers were selected by a clustering analysis. The lowest energy structures were examined in order to determine which face of the reactive π-bond was exposed to the periphery. Structures that exposed the π-face to the periphery leading to the observed product were labeled "correct" while structures that exposed the opposite π-face were labeled "incorrect." Structures that exposed both faces to the periphery were labeled "ambiguous."[184] The energy gap between the best correct and best incorrect structure ("$E_{rel}$") was calculated and compared to the experimentally observed stereoselectivity. The MM method was faster, requiring about a day, while the MM-DFT method was slower, requiring about a week.[185]

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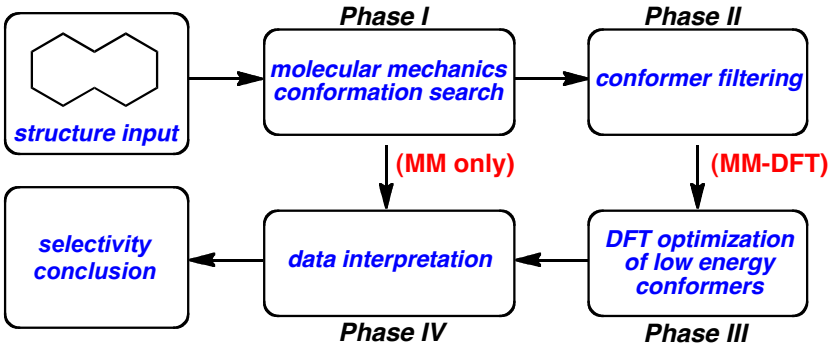
[184] To limit bias during the visual inspection of a macrocycle and to assess ambiguity more rigorously, we suggest analyzing the angle formed by the C–H bond of a reacting endocyclic olefin for example or the C–O bond of a carbonyl function and an atom directly across the macrocycle. If this angle exceeds 140º, the conformer is considered ambiguous.

**Scheme 5.17** Overview of the conformational analysis procedures developed in this study.




## IV. Examples Included in the Study

We examined four different implementations of the approach: MM (OPLS 2005, gas phase), MM-DFT (B3LYP/6-31g(d), gas phase), MM-DFT (B3LYP/6-31g(d), SMD), and MM-DFT (M06-2X/6-31g(d), SMD). Each was carried out on a dataset of 34 examples of intermolecular reactions on chiral macrocycles (Chart 5.1), spanning a wide range of ring sizes (9–22 membered) and reaction types, including electrophilic olefin epoxidations (9 cases), organocuprate additions (6 cases), hydrogenations (6 cases), and 1,2-additions to ketones (7 cases). For continuity, eight cases are medium-sized rings originally considered by Still and co-workers (**5.7**–**5.10**, **5.14**, **5.15**, **5.19**).[179] Only reactions whose products were definitively characterized by NMR spectroscopy, X-ray diffraction, or comparison to authentic material were considered. In 28 cases, one predominant stereoisomer was observed; in 6 others, the reactions were unselective. Reactions that were reported to give "one predominant product" or greater than 8:1 diastereoselectivity were arbitrarily defined as "highly selective."

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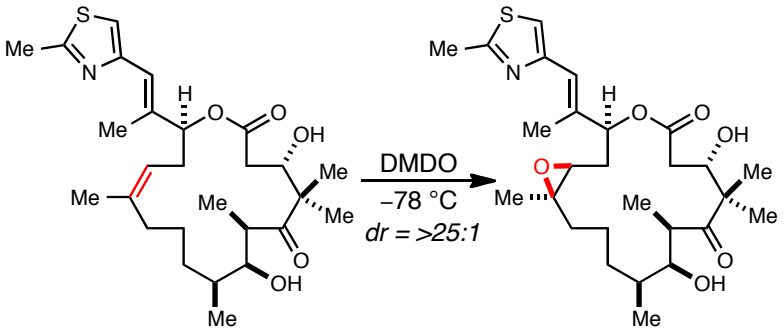
[185] Calculations were performed using Macromodel 9.8 or Gaussian 09. For complete details, please see the supporting information.

## V. Analysis Procedure

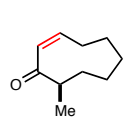
Prior to analysis of the complete dataset, it is instructive to describe the procedure of analysis for a single example initially. Let us consider the results for the case of epothilone B (Scheme 5.18). Here, epoxidation of **5.32** was highly selective (>25:1) for **5.39**. A large set of starting material conformers were generated with molecular mechanics, and then refined with DFT. There was a poor correlation between the MM and DFT energies (Figure 5.4, left panel). As a result, the rank-ordering of the energies of the candidate structures underwent substantial changes. Importantly, the DFT global minimum was found from a high MM energy clustered structure, demonstrating the importance of the conformer filtering process (Figure 5.4, right panel). The lowest energy structures that present the correct and incorrect faces of the trisubstituted olefin (with respect to the olefin carbon bearing the methyl group) to the periphery are shown in Figure 5.5 (**5.40** and **5.42**). According to MM-DFT (B3LYP/6-31g(d), gas phase), the best correct structure is favored over the best incorrect structure by 3.2 kcal/mol. Therefore, the reaction was predicted to be selective for diastereomer **5.39**, in agreement with experiment.

**Scheme 5.18** Epoxidation to form epothilone B.[182(r)]

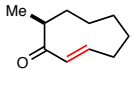



12,13-Desoxyepothilone B, **5.32** Epothilone B, **5.39**

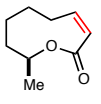
**Chart 5.1** Macrocycles considered in this study. Superscripts refer to the sub-references in [182]. Names are provided to identify the associated target of the macrocycle. Cases in which a natural product was not involved are labeled using the corresponding author involved with the listed publication.



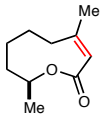
Still *et al.*, **5.7**[a]
cuprate addition



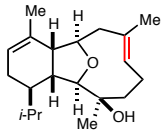
Still *et al.*, **5.8**[a]
cuprate addition



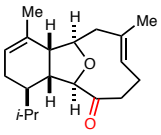
Still *et al.*, **5.9**[a]
cuprate addition



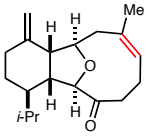
Still *et al.*, **5.10**[a]
hydrogenation



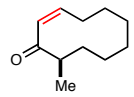
cladiell-11-ene-3,6,7-triol, **5.11**[b]
dihydroxylation



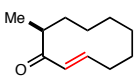
cladiella-6,11-diene-3-ol, **5.12**[b]
ketone addition



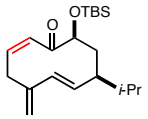
sclerophytin A, **5.13**[c]
epoxidation



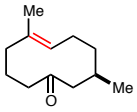
Still *et al.*, **5.14**[a]
cuprate addition



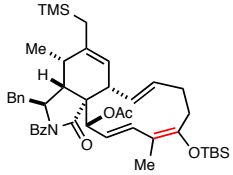
Still *et al.*, **5.15**[a]
cuprate addition



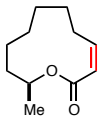
periplanone B, **5.16**[d]
nuc. epoxidation



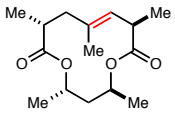
9-deoxy-englerin A, **5.17**[e]
epoxidation



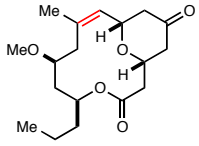
*epi*-cytochalasin D, **5.18**[f]
epoxidation



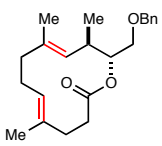
Still *et al.*, **5.19**[a]
cuprate addition



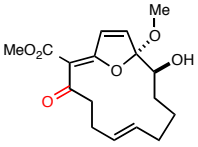
Still *et al.*, **5.20**[g]
hydroboration



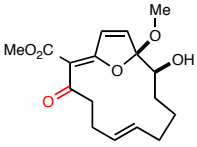
neopeltolide, **5.21**[h]
hydrogenation



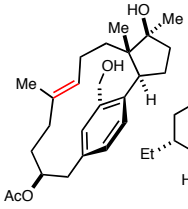
lonomycin A, **5.22**[i]
epoxidation



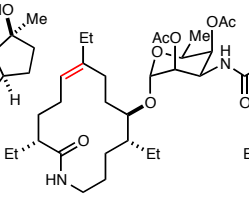
bielschowskysin, **5.23**[j]
hydride reduction



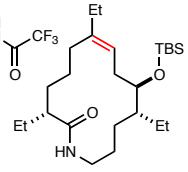
bielschowskysin, **5.24**[j]
hydride reduction



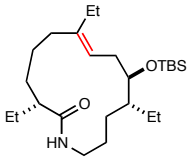
Blume *et al.*, **5.25**[k]
hydrogenation



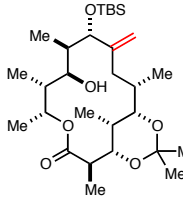
fluvirucin $B_1$, **5.5**[l]
hydrogenation



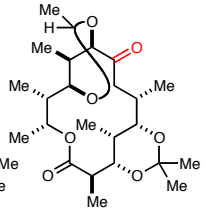
fluvirucin $B_{2\text{-}5}$, **5.26**[m]
hydrogenation



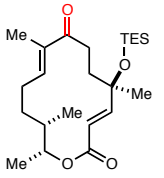
fluvirucin $B_{2\text{-}5}$, **5.27**[m]
hydrogenation



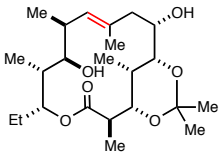
oleandolide, **5.28**[n]
epoxidation



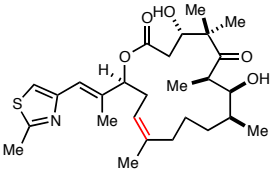
oleandolide, **5.29**[o]
nuc. epoxidation



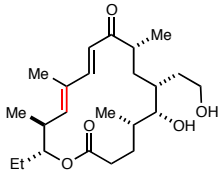
dihydrocineromycin, **5.30**[p]
hydride reduction



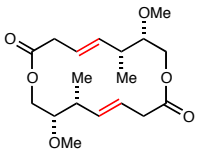
erythronolide B, **5.31**[q]
hydroboration



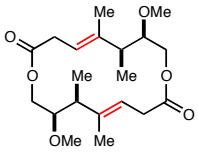
epothilone B, **5.32**[r]
epoxidation



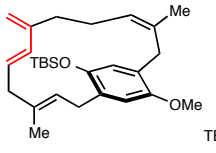
3-deoxyrosaranolide, **5.33**[s]
epoxidation



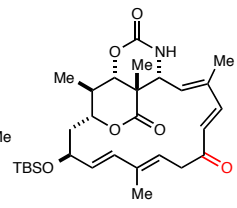
Porco *et al.*, **5.34**[t]
epoxidation



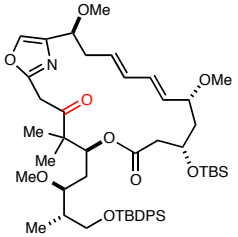
Porco *et al.*, **5.35**[t]
epoxidation



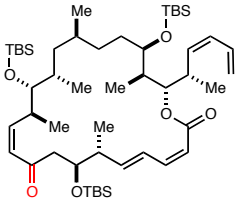
longithorone A, **5.36**[u]
Diels-Alder



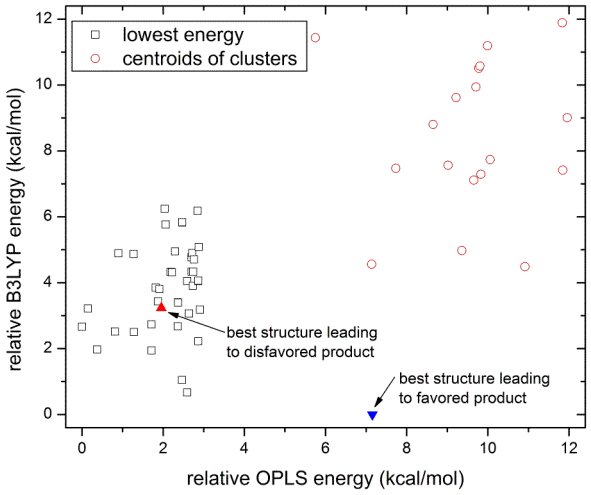
lankacidin C, **5.37**[v]
hydride reduction



monorhizopodin, **5.38**[w]
hydride reduction



dictyostatin, **5.4**[x]
hydride reduction




| *Molecular Mechanics*[a] | | *DFT*[b] | |
|---|---|---|---|
| **Conformer** | **$E_{rel}$ (kcal/mol)** | **Conformer** | **$E_{rel}$ (kcal/mol)** |
| low_1 | 0.00 | cluster_3 | 0.00 |
| low_2 | 0.15 | low_26 | 0.67 |
| low_3 | 0.37 | low_22 | 1.05 |
| low_4 | 0.81 | low_9 | 1.94 |
| low_5 | 0.89 | low_37 | 2.23 |
| low_6 | 1.27 | low_7 | 2.50 |
| low_7 | 1.28 | low_4 | 2.52 |
| low_8 | 1.71 | low_1 | 2.66 |
| low_9 | 1.71 | low_19 | 2.68 |
| low_10 | 1.81 | low_8 | 2.73 |

**Figure 5.4** Results for epothilone B precursor (**5.32**). "low_1" represents the lowest energy structure found by MM; "low_2" represents the second lowest energy structure; etc. "cluster_3" denotes the third lowest energy structure of the clustered set. Poor correlation is observed between the MM and DFT energies (left panel). Substantial shuffling of the energy rank-ordering from MM to DFT (right panel). [a]MM calculations were performed using the OPLS force field. [b]DFT calculations were performed using the B3LYP/6-31G(d) density functional with implicit solvation (SMD).

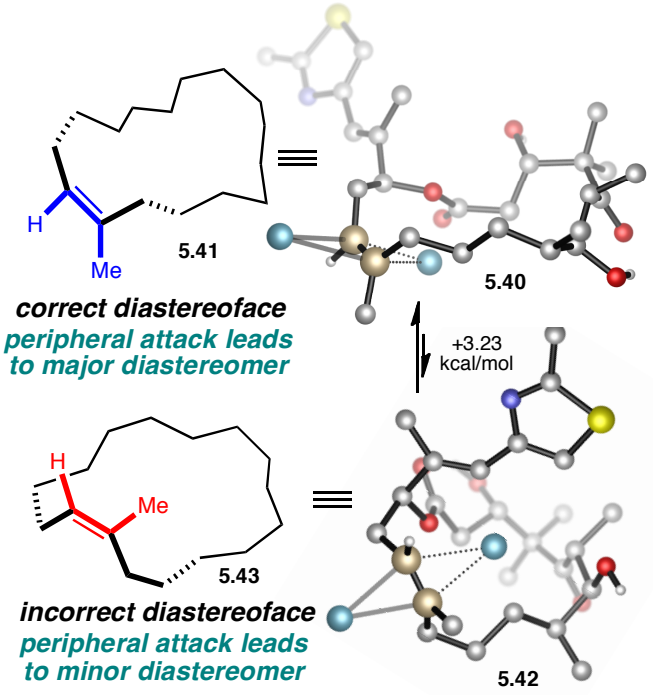



**Figure 5.5** Starting material conformations for 12,13-desoxyepothilone B (**5.32**). Gold spheres represent the reacting olefin.

**VI. Bulk Dataset Analysis**

The same analysis procedure described above was carried out for every member of the dataset. The results shown in Table 5.1 include all the cases that fit the criteria for inclusion, regardless of whether the predictions were correct. The dataset was then scrutinized to determine whether the peripheral attack model is useful in the prediction of diastereochemical outcomes in a binary- and magnitude-based capacity. The former refers to whether an $E_{rel}$ value, regardless of magnitude, predicts the predominant product while the latter is a more stringent test that looks for the prediction of the actual level of selectivity observed in a given reaction.

We began our dataset analysis by looking at the binary diastereochemical outcome prediction to determine whether the model is useful for the prediction of the predominant diastereomer. Ignoring the ambiguous cases, MM (OPLS) makes the correct prediction 79% of the time (Table 5.2). MM-DFT (B3LYP/6-31g(d), gas phase) is slightly worse at 73%, which improves to 81% with implicit solvation. Dispersion corrections (M06-2X/6-31g(d), SMD) perform worse at 70%. Recent findings that ground state MM (OPLS) energies and geometries compare favorably to those from high-level DFT calculations may offer an explanation for why the use of the more expensive MM-DFT methods gives little improvement.[186] Regardless, the accuracies of these predictions are well above 50% (i.e., random guessing), but distant from a range that would invoke a feeling of confidence (>90%), especially given the high-risk associated with these often late-stage transformations.

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[186] Paton, R. S.; Goodman, J. M. *J. Chem. Inf. Model.* **2009**, *49*, 944-955.

**Table 5.1** Conformational analysis of the entire dataset.

| Structure | Ring Size | Associated Target/ Researchers | Reaction | Solvent System | Observed Selectivity | MM[a] | | MM-DFT (B3LYP, gas phase)[b] | | MM-DFT (B3LYP, SMD solvation)[b] | | MM-DFT (M06-2X, SMD solvation)[c] | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Prediction | $E_{rel}$[d] | Prediction | $E_{rel}$[d] | Prediction | $E_{rel}$[d] | Prediction | $E_{rel}$[d] |
| **5.7** | 9 | Still *et al.* | cuprate addition | $Et_2O$ | 24:1 | Correct | 0.86 | Correct | 2.37 | Correct | 2.39 | Correct | 1.81 |
| **5.8** | 9 | Still *et al.* | cuprate addition | $Et_2O$ | 99:1 | Incorrect | –2.40 | Incorrect | –2.98 | Incorrect | –3.01 | Incorrect | –2.86 |
| **5.9** | 9 | Still *et al.* | cuprate addition | $Et_2O$ | 99:1 | Correct | 3.76 | Correct | 2.14 | Correct | 2.03 | Correct | 1.17 |
| **5.10** | 9 | Still *et al.* | hydrogenation | MeOH | 16:1 | Correct | 3.57 | Correct | 1.50 | Correct | 1.60 | Correct | 1.36 |
| **5.11** | 9 | cladiellene | dihydroxylation | $THF/H_2O$ | high[e] | Correct | 4.91 | Correct | 1.94 | Correct | 1.08 | Correct | 3.09 |
| **5.12** | 9 | cladiellene | ketone addition | THF | high[e] | Correct | 7.56 | Correct | 6.75 | Correct | 5.91 | Correct | 5.08 |
| **5.13** | 9 | sclerophytin A | epoxidation | $CHCl_3$ | 1.8:1 | Correct | 1.66 | Correct | 1.90 | Correct | 0.95 | Correct | 1.88 |
| **5.14** | 10 | Still *et al.* | cuprate addition | $Et_2O$ | 32:1 | Correct | 1.60 | Correct | 0.56 | Correct | 0.28 | Incorrect | –0.34 |
| **5.15** | 10 | Still *et al.* | cuprate addition | $Et_2O$ | 16:1 | Incorrect | –0.36 | Correct | 0.38 | Incorrect | –0.01 | Incorrect | –0.79 |
| **5.16** | 10 | periplanone B | nuc. epoxidation | THF | 4:1 | Correct | 1.93 | Incorrect | –1.07 | Correct | 0.62 | Incorrect | –1.10 |
| **5.17** | 10 | deoxyenglerin A | epoxidation | $CH_2Cl_2$ | high[e] | Correct | 1.83 | Correct | 4.62 | Correct | 4.65 | Correct | 3.55 |
| **5.18** | 11 | cytochalasin D | epoxidation | $CHCl_3$ | >20:1 | Correct | 2.90 | Correct | 3.14 | Correct | 4.01 | Correct | 3.42 |
| **5.19** | 11 | Still *et al.* | cuprate addition | $Et_2O$ | 24:1 | Correct | 2.38 | Correct | 1.79 | Correct | 1.60 | Correct | 1.58 |
| **5.20** | 12 | Still *et al.* | hydroboration | THF | >9:1 | Correct | 4.10 | Correct | 4.16 | Correct | 4.05 | Correct | 3.49 |
| **5.21** | 12 | neopeltolide | hydrogenation | EtOH | >9:1 | Correct | 1.63 | Correct | 0.54 | Correct | 0.80 | Correct | 1.43 |
| **5.22** | 12 | lonomycin A | epoxidation | $CH_2Cl_2$ | 9:1 | Correct | 2.45 | Correct | 2.24 | Correct | 2.34 | Correct | 2.15 |
| **5.23** | 13 | bielschowskysin | hydride reduction | $THF/H_2O$ | high[e] | Incorrect | –1.57 | Incorrect | –2.19 | Incorrect | –1.15 | Incorrect | –2.26 |
| **5.24** | 13 | bielschowskysin | hydride reduction | $THF/H_2O$ | high[e] | Incorrect | –1.23 | Incorrect | –2.77 | Incorrect | –2.41 | Incorrect | –1.43 |
| **5.25** | 14 | blume *et al.* | hydrogenation | MeOH | 8:1 | Correct | 3.20 | Correct | 2.19 | Correct | 3.21 | Correct | 1.77 |
| **5.5** | 14 | fluvirucin $B_1$ | hydrogenation | EtOH | >49:1 | Correct | 0.38 | Correct | 1.04 | Incorrect | ambig. | Incorrect | ambig. |
| **5.26** | 14 | fluvirucin $B_{2\text{-}5}$ | hydrogenation | toluene | 9:1 | Incorrect | 1.18 | Incorrect | –5.13 | Incorrect | –1.48 | Incorrect | ambig. |
| **5.27** | 14 | fluvirucin $B_{2\text{-}5}$ | hydrogenation | toluene | 7:1 | Correct | 0.72 | Correct | 0.89 | Correct | 0.84 | Correct | 0.48 |
| **5.28** | 14 | oleandolide | epoxidation | $CH_2Cl_2$ | high[e] | Incorrect | –3.27 | Incorrect | –3.38 | Incorrect | –5.01 | Incorrect | –2.89 |
| **5.29** | 14 | oleandolide | nuc. epoxidation | THF/DMSO | >32:1 | Correct | 3.05 | Incorrect | –0.15 | Correct | 1.89 | Correct | 2.20 |
| **5.30** | 14 | dihydrocineromycin | hydride reduction | $MeOH/CH_2Cl_2$ | high | Incorrect | –0.08 | Incorrect | ambig. | Correct | 1.82 | Correct | 1.21 |
| **5.31** | 14 | erythronolide B | hydroboration | THF | 9:1 | Correct | 0.93 | Correct | 6.91 | Correct | 6.05 | Correct | 6.98 |
| **5.32** | 16 | epothilone B | epoxidation | $CH_2Cl_2$ | >25:1 | Correct | 1.87 | Correct | 0.82 | Correct | 3.23 | Incorrect | –1.36 |
| **5.33** | 16 | deoxyrosaranolide | epoxidation | $CH_2Cl_2$ | >15:1 | Correct | 1.38 | Correct | 4.61 | Correct | 4.78 | Correct | 0.87 |
| **5.34** | 16 | Porco *et al.* | epoxidation | $CCl_4$ | 2.5:1 | Correct | 1.89 | Correct | 3.59 | Correct | 4.13 | Correct | 2.96 |
| **5.35** | 16 | Porco *et al.* | epoxidation | $CH_2Cl_2$ | high[e] | Correct | 2.77 | Correct | 1.23 | Correct | 2.09 | Correct | 1.86 |
| **5.36** | 16 | longithorone A | Diels–Alder | $CH_2Cl_2$ | 1.4:1 | Correct | ambig. | Correct | ambig. | Correct | ambig. | Correct | ambig. |
| **5.37** | 17 | lankacidin C | hydride reduction | MeOH | unselec. | Correct | ambig. | Correct | ambig. | Correct | 0.29 | Correct | ambig. |
| **5.38** | 19 | monorhizopodin | hydride reduction | MeOH | high[e] | Correct | 0.10 | Incorrect | –1.36 | Correct | 0.07 | Correct | 3.12[f] |
| **5.4** | 22 | dictyostatin | hydride reduction | EtOH | high[e] | Correct | 0.41 | Incorrect | ambig. | Incorrect | ambig. | Incorrect | –0.29[f] |

[a] OPLS-2005 [b] B3LYP/6-31g(d) [c] M06-2X/6-31g(d) [d] kcal/mol [e] The selectivity was high, but not specified. [f] M06-2X/6-31g(d) // M06-L/6-31g(d)

**Table 5.2** Accuracy of predicting the major product (regardless of $E_{rel}$).

| Method | % correct (all $E_{rel}$) | % correct ( $\|E_{rel}\|$ > 1 kcal/mol) |
|---|---|---|
| MM only (gas phase) | 79 | 78 |
| B3LYP (gas phase) | 73 | 71 |
| B3LYP (SMD solvation) | 81 | 78 |
| M06-2X (SMD solvation) | 70 | 76 |

Given the lackluster accuracy from the binary test for selectivity, it was expected that a more stringent test for the prediction of magnitude would be similarly mediocre. Indeed, Table 5.3 indicates that $E_{rel}$ values are not well correlated with the observed selectivities. Even when the analysis is restricted to substrates with $|E_{rel}|$ values of greater than 1.0 kcal/mol (a screen for high selectivity), successful prediction is achieved 67% and 74% of the time for MM and MM-DFT respectively. One can also ask whether macrocycles with small biases ($|E_{rel}|$ < 1.0 kcal/mol) or ambiguous global minima tend to give unselective reactions. The data clearly reveal that neither finding is meaningful. A rationalization for this particularly poor correlation is that unbiased substrates can still give high levels of stereoselectivity through transition state effects, which are not accessible via the ground state-based peripheral attack model.

**Table 5.3** Accuracy of predicting the level of selectivity.

(a)

| observed *dr* | MM only $\|E_{rel}\|$ (kcal/mol) ambig. | 0.0 – 1.0 | > 1.0 |
|---|---|---|---|
| > 8 : 1 | 0 | 6 | 16 |
| < 1 : 8 | 0 | 1 | 5 |
| 8 : 1 – 1 : 8 | 2 | 1 | 3 |
| **total** | 2 | 8 | 24 |
| **accuracy**[a] | 100 % | 13 % | 67 % |

(b)

| observed *dr* | solv. B3LYP $\|E_{rel}\|$ (kcal/mol) ambig. | 0.0 – 1.0 | > 1.0 |
|---|---|---|---|
| > 8 : 1 | 2 | 3 | 17 |
| < 1 : 8 | 0 | 1 | 5 |
| 8 : 1 – 1 : 8 | 1 | 4 | 1 |
| **total** | 3 | 8 | 23 |
| **accuracy**[a] | 33 % | 13 % | 74 % |

[a] the number of compounds with the correct sense of selectivity divided by the total in the specified range.

## VII. Subsets of the Complete Dataset

The poor correlation between observed and predicted selectivity clearly indicate that the peripheral attack model cannot be universally applied with confidence. This is a startling conclusion given its widespread adoption, however, it is quite possible that particular systems are better suited for the model than others. With this possibility in mind, we attempted to break up the dataset into subsets, which include macrocycle size, olefin orientation, and reaction type.

*Macrocycle Type and Olefin Orientation*. A key goal of this study was to determine whether the peripheral attack model is applicable to large macrocycles (>10-12 membered), given that they potentially are more flexible than the smaller rings for which the model was originally proposed. Table 5.4 shows that large macrocycles perform well (88% binary accuracy) when compared to the 11-14 membered ring subset and roughly equivalent when compared to the 9 and 10 membered ring subset. The ground state biases of both E and Z intra-annular olefins appear to translate to observed stereoselectivity in an equal fashion (Table 5.5), however in each of these cases the observed accuracies are below a high confidence threshold. Overall, data from both Table 5.4 and Table 5.5 do not reveal any particular scenario in which the peripheral attack model is more reliable, further raising concerns regarding its utility.

**Table 5.4** Accuracy of the peripheral attack model by ring size.

| ring size | # of cases | accuracy[a] (major product) | accuracy[b] (high selectivity) |
|---|---|---|---|
| 9 and 10 | 11 | 9 of 11 (82%) | 6 of 7 (86%) |
| 11–14 | 15 | 10 of 15 (67%) | 8 of 12 (67%) |
| >15 | 8 | 7 of 8 (88%) | 3 of 4 (75%) |

[a] MM-DFT (B3LYP/6-31g(d), SMD) [b] $|E_{rel}| > 1.0$ kcal only

**Table 5.5** Accuracy of the peripheral attack model by olefin orientation.

| olefin type | # of cases | accuracy[a] (major product) | accuracy[b] (high selectivity) |
|---|---|---|---|
| E-intra-annular | 14 | 11 of 14 (79%) | 9 of 11 (82%) |
| Z-intra-annular | 11 | 9 of 11 (82%) | 6 of 7 (86%) |
| 1,1'-extra-ann. | 1 | 0 of 1 (0%) | 0 of 1 (0%) |

[a] MM-DFT (B3LYP/6-31g(d), SMD) [b] $|E_{rel}| > 1.0$ kcal only

*Reaction Subsets.* Implicit to the peripheral attack mode is the lack of reaction or reagent consideration, suggesting that the accuracy of its predictions might vary with reaction type (Table 5.6). When the bulk dataset is categorized by reaction type, the first hint of a useful model emerges. In particular, epoxidation reactions stand out as reliably predicted reactions in both a binary and magnitude-based manner in all but one case. This one outlying case, **5.28**, likely proceeds via a hydroxyl-directed mechanism thus accessing an otherwise inaccessible face of the olefin (Figure 5.6).[182(n)] It is therefore suggested that if DMDO were used for this epoxidation, peripheral attack would have constituted the major reaction pathway.

**Table 5.6** Accuracy of the peripheral attack model by reaction type.

| reaction type | # of cases | accuracy[a] (major product) | accuracy[b] (high selectivity) |
|---|---|---|---|
| epoxidation | 9 | 8 of 9 (89%) | 7 of 8 (88%) |
| cuprate add. | 6 | 4 of 6 (67%) | 3 of 4 (75%) |
| hydrogenation | 6 | 4 of 6 (67%) | 1 of 2 (50%) |
| 1,2-addition | 6 | 4 of 6 (67%) | 2 of 4 (50%) |

[a] MM-DFT (B3LYP/6-31g(d), SMD) [b] $|E_{rel}| > 1.0$ kcal only

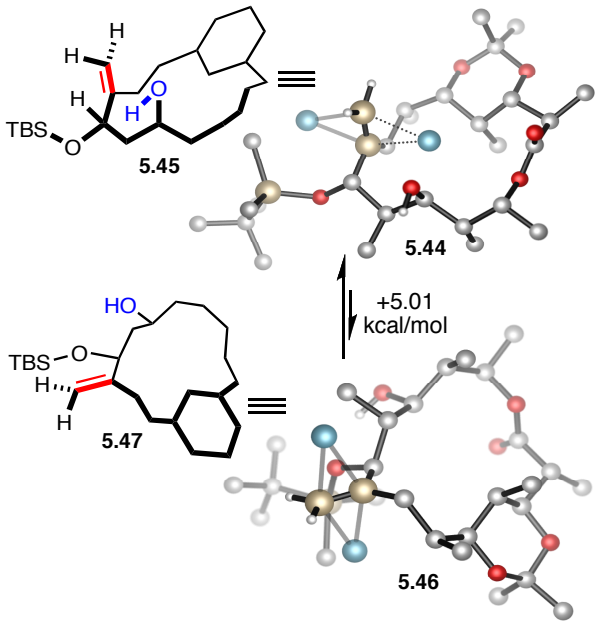


**Figure 5.6** Conformational analysis of the oleandolide precursor **5.28** reveals the possibility for a hydroxyl-directed reaction with *m*-CPBA.[182(n)]

The conjugate addition of cuprate reagents represents a higher level of transition state complexity compared with olefin epoxidations. Assuming that the initial addition of the reagent is both irreversible and selectivity determining, then the corresponding stereoelectronic requirement should be that the carbonyl group and the olefin of the enone be in conjugation. However, no such constraint is applied in the peripheral attack model. Therefore, the ground state macrocyclic conformations may not necessarily be relevant to the transition states for cuprate addition. Indeed, it is noteworthy that Still and co-workers considered developing strain in the product to be responsible for failures of the

model.[179] Furthermore, recent studies suggest that it is a subsequent reductive elimination step, rather than the initial addition, that may be both rate and selectivity determining.[187]

Although the hydrogenation of macrocyclic olefins might appear to be mechanistically simpler than cuprate additions, the performance of the peripheral attack model is similarly poor. This highlights another deficiency of the peripheral attack model, which involves the assumption that the structure of the starting material is fixed. Since intermediate catalyst-substrate complexes may significantly perturb conformational biases, ground state conformations may be irrelevent.

The 1,2-addition of organometallic reagents to macrocyclic ketones is yet another challenging case for the peripheral attack model. Although previous studies[188] have suggested that these reactions occur through relatively early transition states, the work of Tomoda and co-workers[189] now suggests that sodium borohydride reductions may actually proceed via very late transition states such that interior attack becomes quite plausible. Further, stereoelectronic effects are ignored by the peripheral attack model in a similar fashion to cuprate additions. Specifically, the Felkin-Anh model[190] assumes that the transition state for addition involves an antiperiplanar alignment between the forming bond and the best hyperconjugative acceptor adjacent to the carbonyl group, regardless of which rotamer is dominant in the ground state. In contrast, the peripheral attack model

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[187] (a) Luibrand, R. T.; Taigounov, I. R.; Taigounov, A. A. *J. Org. Chem.* **2001**, *66*, 7254-7262. (b) Mori, S.; Nakamura, E. *Chem. Eur. J.* **1999**, *5*, 1534-1543. (c) Kireev, A. S.; Manpadi, M.; Kornienko, A. *J. Org. Chem.* **2006**, *71*, 2630-2640.

[188] (a) Chérest, M.; Felkin, H. *Tet. Lett.* **1968**, *18*, 2205-2208. (b) Ashby, E. C.; Noding, S. A.; *J. Am. Chem. Soc.* **1976**, *98*, 2010-2011.

[189] Yasumitsu, S.; Kaneno, D.; Tomoda, S. *J. Phys. Chem. A.* **2009**, *113*, 2578-2583.

assumes that the ground state conformations are also the reactive ones. As a result, the accuracy for 1,2-additions suffers.

Another explanation for the low predictability of 1,2-additions is that the model does not consider the metal ion or the size of the nucleophile. With chelating metals, it is possible that the conformations of relatively polar macrocycles might be perturbed. For example, in the case of monorhizopodin intermediate **5.38**, a significant turnover in selectivity was observed when Ce(III) was introduced to the reaction. With respect to reagent size, it is conceivable that small reagents may be able to access the interior face of large macrocycles, leaving a core assumption of the peripheral attack model intrinsically flawed.

**VIII. Conclusions**

The work described in this chapter reveals a two-part project aimed at the analysis of the peripheral attack model. The first part was the development of a computational protocol and tool for application of the peripheral attack model. This has been completed in very thorough fashion by comparing parallel protocols that utilize MM or both MM and DFT with various additional parameters. Using this computational tool, we turned to the second aspect of the project, which is the evaluation of the accuracy and utility of the model.

In light of the poor predictability associated with conjugate additions, hydrogenations, and 1,2-additions, we conclude that the peripheral attack model should no longer be used outside of epoxidations. Since stereocontrol in the context of a macrocyclic sub-

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[190] (a) Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, *1*, 61. (b) Anh, N. T.; Eisenstein, O.; Lefour, J-M.; Dau, M-E. *J. Am. Chem. Soc.* **1973**, *95*, 6146-6147.

strate is intrinsically late-stage and high risk, full transition state analysis should be performed if risk-reduction is considered necessary. Parameterization of the model by distinguishing each case in terms of reaction type, reagent size, macrocycle size or olefin orientation could further improve the accuracy of the model, but fundamentally the peripheral attack model is an old model fraught with too many compromising assumptions. Computational chemistry has advanced tremendously since the initial periplanone synthesis, and we must now step fully into the transition state era for semi-quantitative stereochemical prediction.

# *Chapter 5*

## IX. Supporting Information

### A. Computational Methods

*General Overview.* Our study examined two types of computational procedures for implementing the peripheral attack model: one involving only molecular mechanics ("MM") and one involving molecular mechanics followed by further optimization using DFT ("MM-DFT"). In both cases, the conformational space of an arbitrary macrocycle bearing a reactive π-bond was first searched. Then, the structures were optimized to local minima. The lowest energy structures were examined to determine which face of the reactive π-bond was exposed to the periphery. Finally, the energy gap between the best structure that preferentially exposed one face and the best structure that exposed the opposite face ("$E_{rel}$") was calculated and compared to the experimentally observed stereoselectivity.

*Requirements.* The MM method was faster, requiring about a day, while the MM-DFT method was slower, requiring about a week. These estimated times are based on using one core of a standard desktop computer (Intel Core i5 processor; Model 650, Dual Core,

3.20 GHz) for MM calculations and eight 8-core nodes simultaneously for DFT calculations (Intel Xeon E5520 processors; 2.26 GHz with 24 GB RAM).

*Phase I: Molecular Mechanics.* 120,000 candidate geometries were generated and optimized for the reactant macrocycle (only structures within 12 kcal/mol of the global minimum were kept). Then, the structures were superimposed and any redundant conformers were removed (all heavy atoms were considered at a discard criterion of 0.5 Å RMSD).

*Phase II: Conformer Filtering.* (MM-DFT only.) Because refinement of all the structures produced by Phase I with DFT methods would have been prohibitively time-consuming, the lowest energy conformers and some representative higher energy conformers were selected for optimization. If the number of remaining conformers was less than or equal to 60, then all of the conformers were subjected to further DFT optimization. If the remaining number of conformers exceeded 60, then the 40 lowest energy structures (MM energies) were selected for further DFT optimization. Then, the following filtering process was used to select a further set of representative geometries. First, a more restrictive redundant conformer elimination was performed (macrocycle heavy atoms only at a discard criterion of 0.5 Å RMSD). RMSD-based clustering was then performed (macrocycle atoms only) on the resulting subset creating up to 20 clusters (based on choosing the minimum in the Kelley penalty function). The structures nearest the centroid of each cluster (in RMSD space) were also selected for further optimization.

*Phase III: Density Functional Theory.* (MM-DFT only.) Each structure was minimized with DFT methods (details below). The resulting geometries were verified to be true local minima by standard frequency analysis.

*Phase IV: Interpretation.* The resulting structures were ranked by energy. Structures that exposed the π-face to the periphery that would lead to the observed product were labeled "correct" while structures that exposed the opposite π-face were labeled "incorrect." Structures that exposed both faces to the periphery were labeled as "ambiguous." The energy difference between the best correct and best incorrect structure, $E_{rel}$, was computed. Positive values of $E_{rel}$ were defined to mean that the best correct structure was lower in energy than the best incorrect structure (i.e., agreement between theory and experiment). No $E_{rel}$ values were assigned to macrocycles with ambiguous global minima. Some structures had a correct or incorrect global minimum, followed by a series of similarly disposed structures leading up to an ambiguous structure. In those cases, $E_{rel}$ was defined as the energy of the ambiguous structure relative to that of the global minimum with the same sign convention as above.

*Molecular Mechanics.* All calculations were performed using Macromodel (Version 9.8) interfaced to the Maestro program (Version 9.1).[191] All conformational searches were performed with the Monte Carlo Multiple Minimum (MCMM) method.[192] Since it has been suggested that low-mode-based searching is a potentially superior search method,[193] some of the conformational searches were repeated with a tandem molecular dynamics-large scale low-mode-based method.[194] However, in our hands, this did not give superior

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[191] Mohamadi, F.; Richards, N. G.; Guida, W. C.; Liskamp, R.; Lipton, M.; Caufield, C.; Chang, G.; Hendrickson, T.; Still, W. C. *J. Comput. Chem.* **1990**, *11*, 440-467.

[192] Chang, G.; Guida, W. C.; Still, W. C. *J. Am. Chem. Soc.* **1989**, *111*, 4379-4386.

[193] (a) Parish, C.; Lombardi, R.; Sinclair, K.; Smith, E.; Goldberg, A.; Rappleye, M.; Dure, M. *J. Mol. Graphics and Modelling*. **2002**, *21*, 129-150. (b) Labute, P. *J. Chem. Inf. Model.* **2010**, *50*, 792-800. (c) Kolossváry, I.; Keseru, G. M. *J. Comp. Chem.* **2001**, *22*, 21.

[194] Schrodinger monthly newsletter, January 2011. https://www.schrodinger.com/upload/Schrodinger_Newsletter_Jan2011.pdf (accessed August 5, 2011).

results and was not used further. The OPLS-2005 force field, which is an improved version of the authentic[195] OPLS force field, was chosen for MM energies. This force field was attractive because it is specifically parameterized for organic liquids[196] and has high quality torsional parameters for most commonly occurring organic functional groups. Although OPLS-type forcefields also give superior GB/SA solvation energies,[197] it was ultimately found that solvation at the MM stage did not improve the quality of the results, but did increase the computational cost by a factor of three to four times. Therefore, no solvation was applied at the MM stage for any protocol (a constant dielectric of 1.0 was applied).

All reasonable torsion angles were varied, including those of amide, ester, and silyl bonds. Optimizations were performed using the TNCG algorithm[198] (convergence criterion set to 0.05 kJ/mol). Redundant conformer eliminations were performed in Maestro (based on geometries only; energies were ignored). Conformer clustering (for the MM-DFT protocol only) was performed using the Conformer Cluster script in Maestro. This script first generated a matrix that related all of the structures by RMSD. Then, an algorithm sorted the structures into clusters such that intracluster distances (in RMSD space) were minimized while intercluster distances were maximized. The structures nearest the centroid of each cluster were selected for further DFT refinement. In general, these clustered structures were higher in energy and did not duplicate any of the 40 structures already selected for further refinement.

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[197] Reddy, M. R.; Erion, M. D.; Agarwal, A.; Viswanadhan, V. N.; McDonald, D. Q.; Still, W. C. *J. Comp. Chem.* **1998**, *19*, 769-780.

*Density Functional Theory.* All calculations were performed using Gaussian 09 (Revision A.02)[199] on the Odyssey Cluster at Harvard University. Each starting structure, already a local minimum with respect to the MM PES, was re-optimized at B3LYP/6-31g(d),[200] which is relatively inexpensive compared to more modern functionals. However, the performance of B3LYP has recently been called into question, particularly for large organic molecules.[201] These errors seem to be related to the fact that B3LYP treats dispersion interactions as purely repulsive, a problem that is pronounced in branched alkanes.[202] Given that many macrocycles contain branched alkanes, the MM structures were also optimized at M06-2X/6-31g(d).[203] (Larger structures were optimized at M06-2X/6-31g(d)//M06-L/6-31g(d). The semi-local M06-L functional is designed to reproduce main-group thermochemistry and non-covalent interactions while allowing substantial performance enhancements with the use of density fitting basis sets.[204])

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[199] Gaussian 09, Revision A.02: Frisch, M. J.; Trucks. G. W.; Schlegel, H. B.; Scuseria G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann. R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian Inc., Wallingford, CT, **2009**.

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[201] (a) Wodrich, M. D.; Corminboeuf, C.; Schleyer, P. von. R. *Org. Lett.* **2006**, *8*, 3631-3634. (b) Wodrich, M. D.; Corminboeuf, C.; Schreiner, P. R.; Fokin, A. A.; Schleyer, P. von R. *Org. Lett.* **2007**, *9*, 1851-1854. (c) Tirado-Rives, J.; Jorgensen, W. L. *J. Chem. Theory Comput.* **2008**, *4*, 297-306.

[202] (a) Wodrich, M.D.; Jana, D.F.; Schleyer, P. von. R.; Corminboeuf, C. *J. Phys. Chem. A.* **2008**, *112*, 11495-11500. (b) Gonthier, J. F.; Wodrich. M. D.; Steinmann, S. N.; Corminboeuf, C. *Org. Lett.* **2010**, *12*, 3070-3073.

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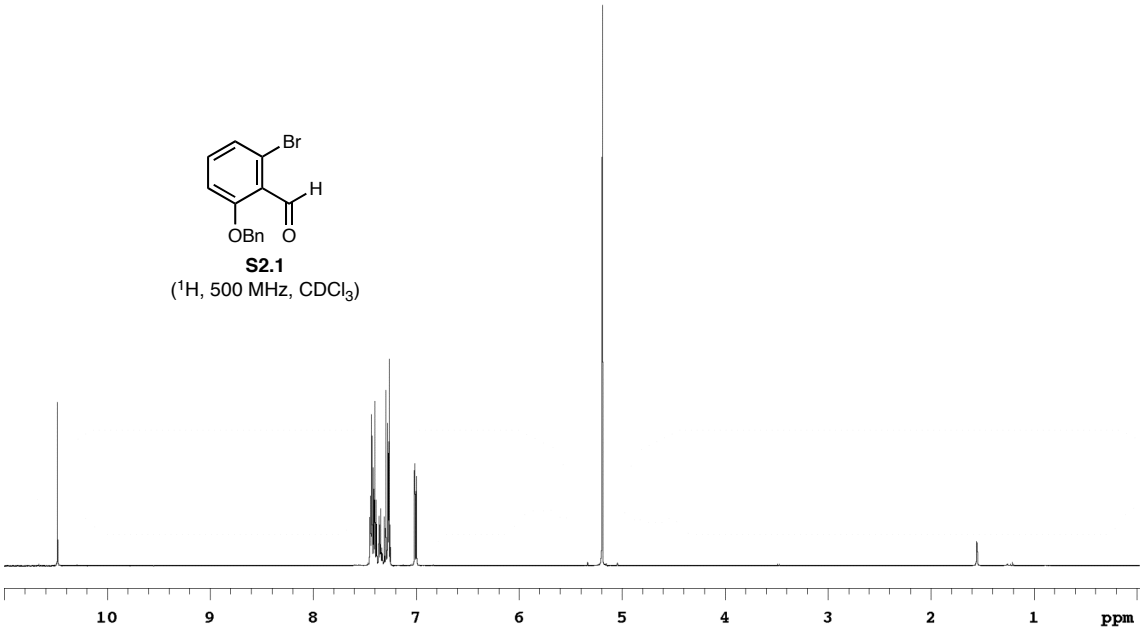
[204] Zhao, Y.; Truhar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101-194118.

$E_{rel}$ values were calculated from free energies at 298.15 K for B3LYP/6-31g(d) and M06-2X/6-31g(d) calculations. Free energy corrections from M06-L were added to single point M06-2X/6-31g(d)//M06-L/6-31g(d) electronic energies for some calculations. The SMD implicit solvation model[205] was used where applicable. In cases where mixed solvent systems were used, calculations were repeated for each component; $E_{rel}$ values did not vary significantly between solvents.

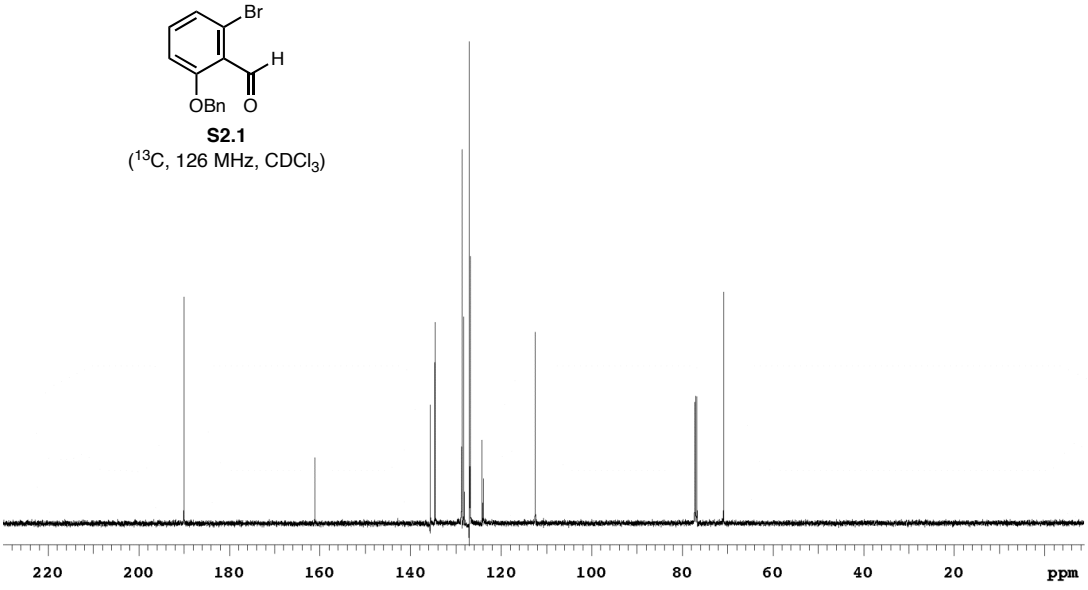
[205] Marenich, A. V.; Cramer. C. J.; Truhlar, D. G. *J. Phys. Chem. B.* **2009**, *113*, 6378-6396.

# *Appendix 1*

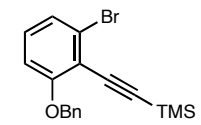
**Catalog of Spectra**




**S2.1**
($^{1}$H, 500 MHz, $CDCl_3$)



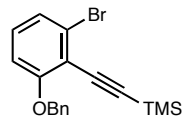

**S2.1**
($^{13}$C, 126 MHz, $CDCl_3$)




**2.14**

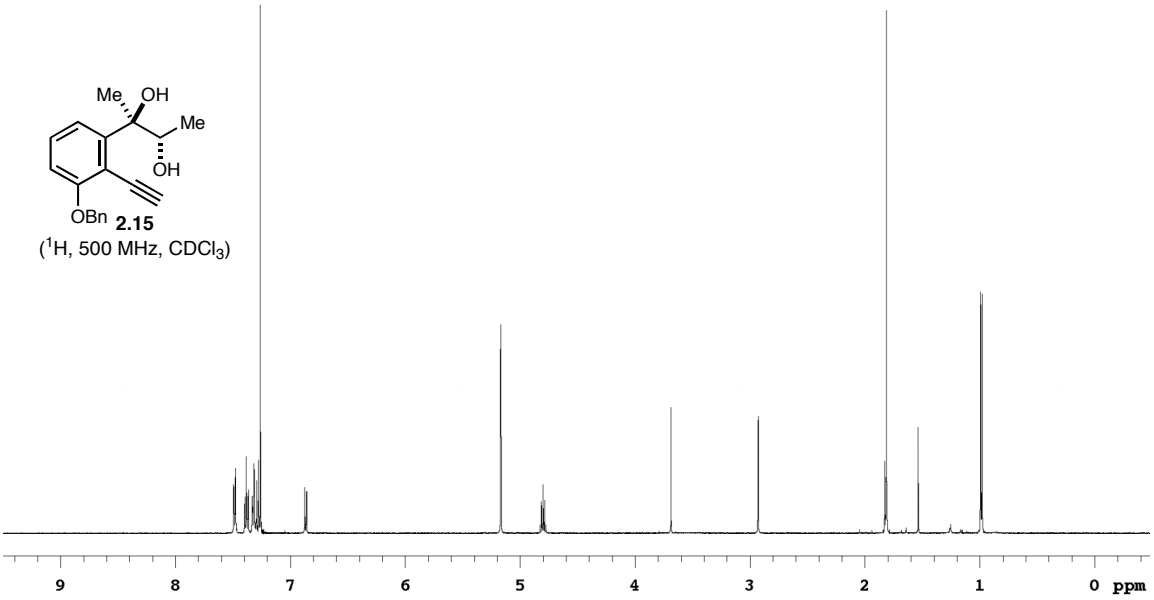
($^1$H, 500 MHz, $CDCl_3$)



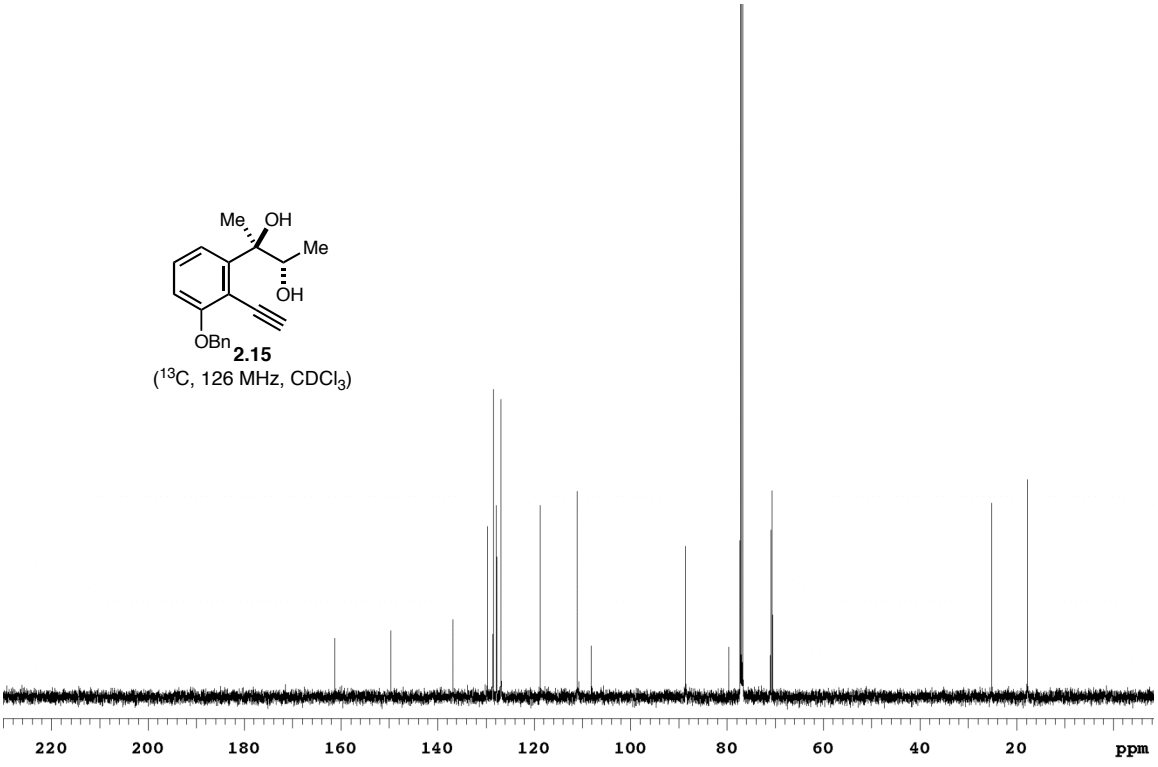

**2.14**

($^{13}$C, 126 MHz, $CDCl_3$)



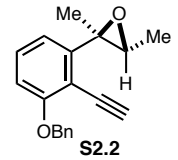

**2.15**

($^1$H, 500 MHz, $CDCl_3$)




**2.15**

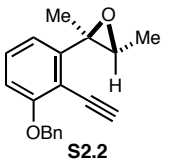
($^{13}$C, 126 MHz, $CDCl_3$)




**S2.2**

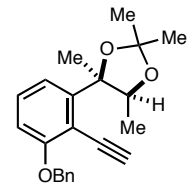
($^1$H, 500 MHz, $CDCl_3$)



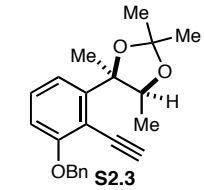

**S2.2**

($^{13}$C, 126 MHz, $CDCl_3$)

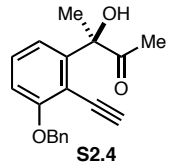



**S2.3**
($^1$H, 500 MHz, $CDCl_3$)



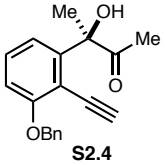

**S2.3**
($^{13}$C, 126 MHz, $CDCl_3$)




**S2.4**

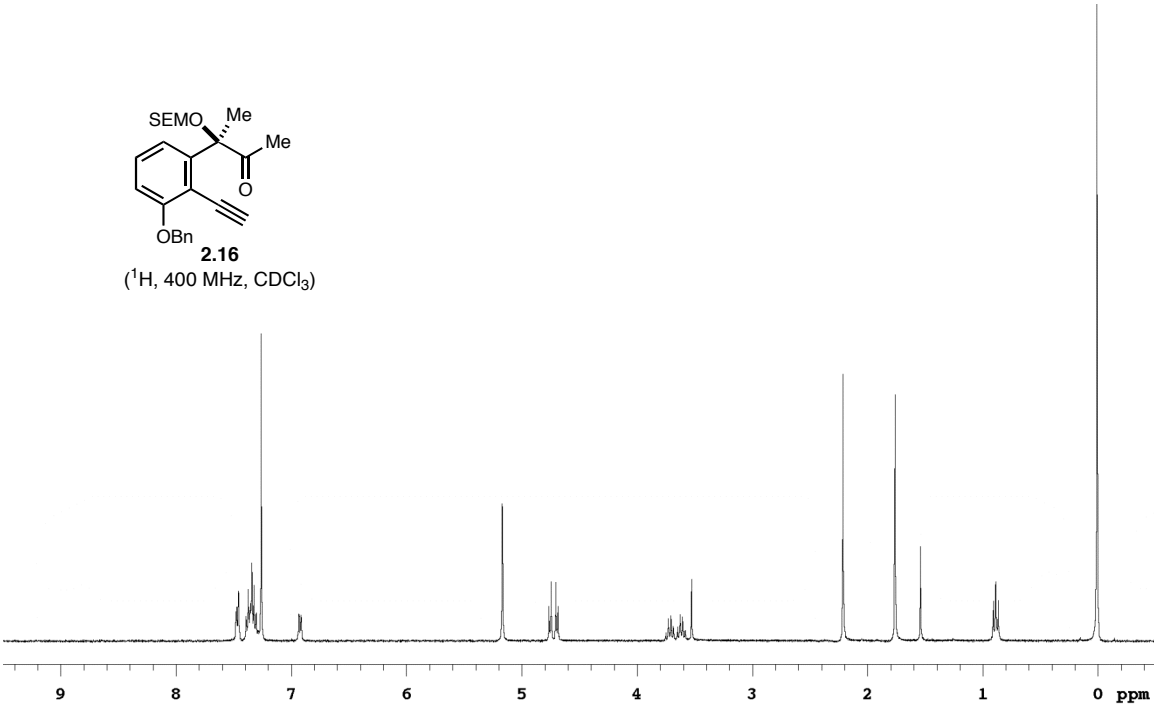
($^1$H, 500 MHz, $CDCl_3$)



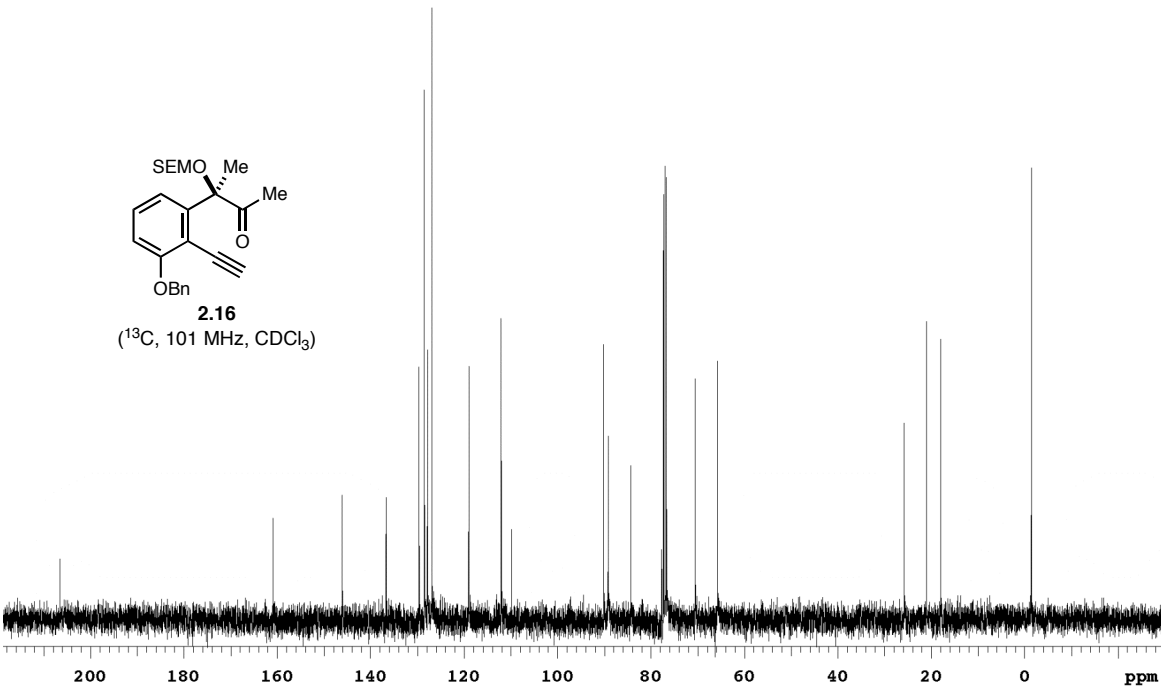




**S2.4**

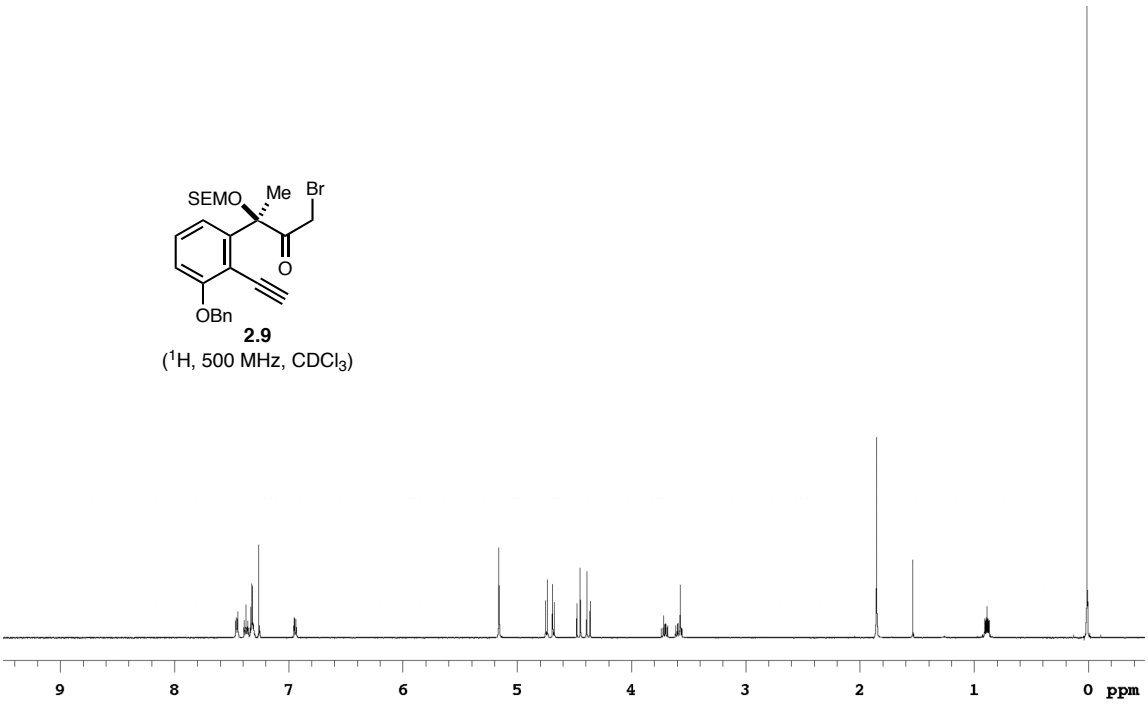
($^{13}$C, 126 MHz, $CDCl_3$)



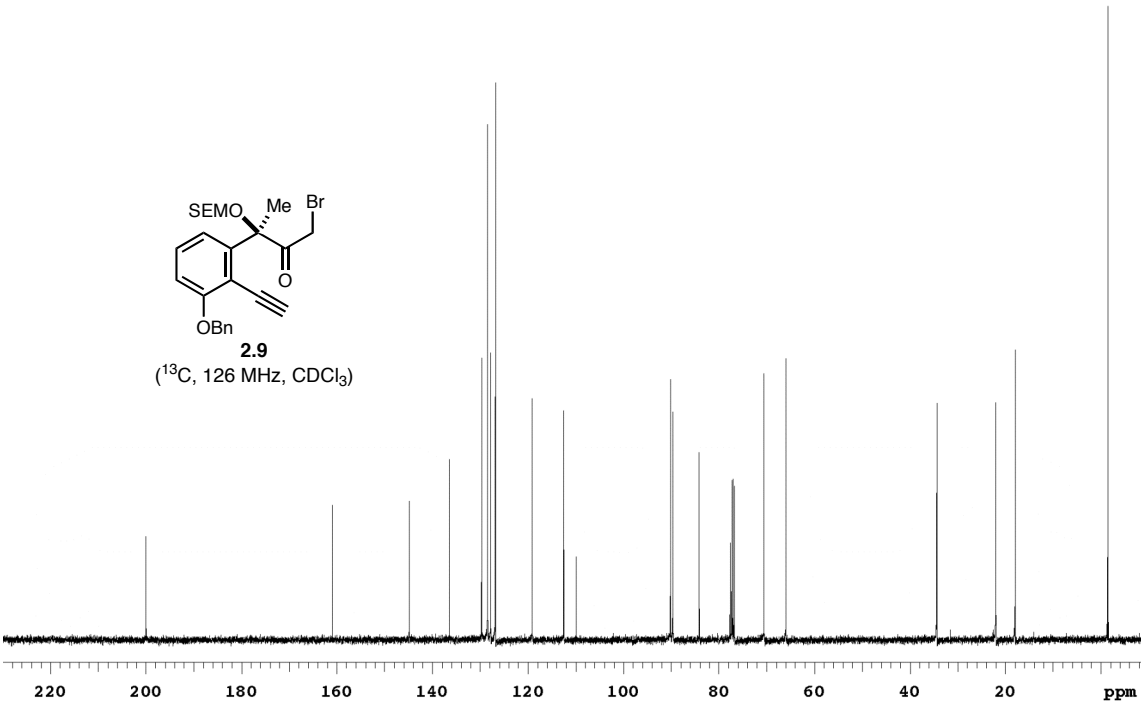

**2.16**
($^1$H, 400 MHz, $CDCl_3$)



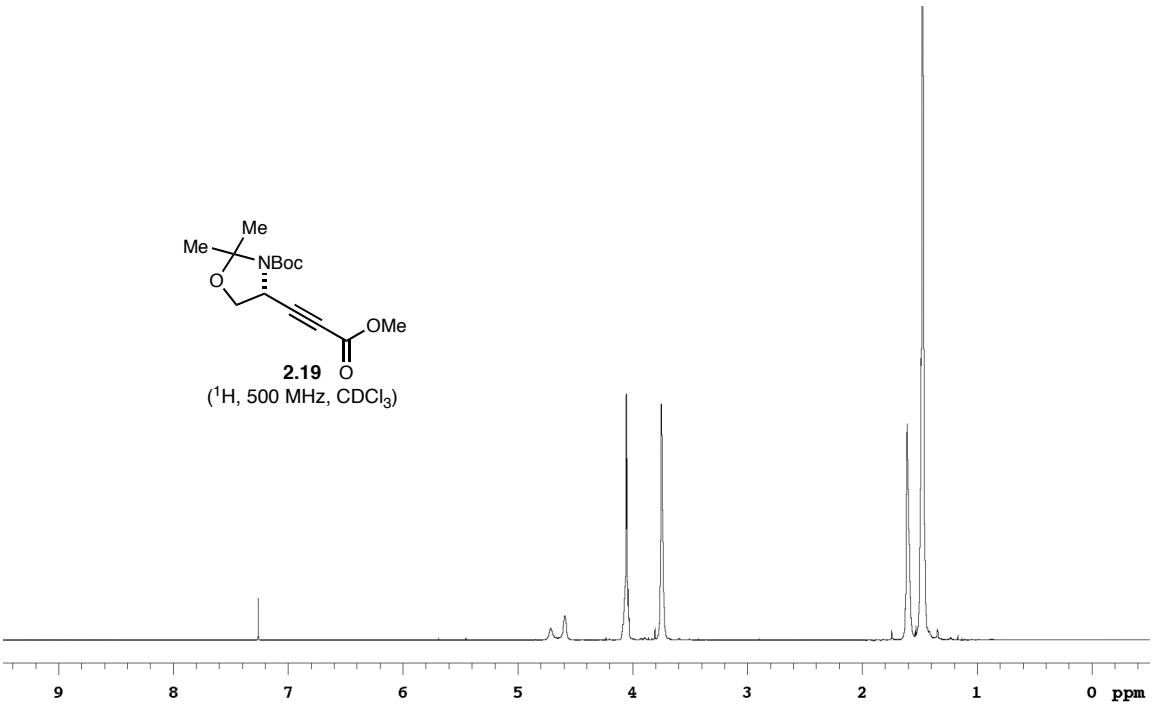

**2.16**
($^{13}$C, 101 MHz, $CDCl_3$)



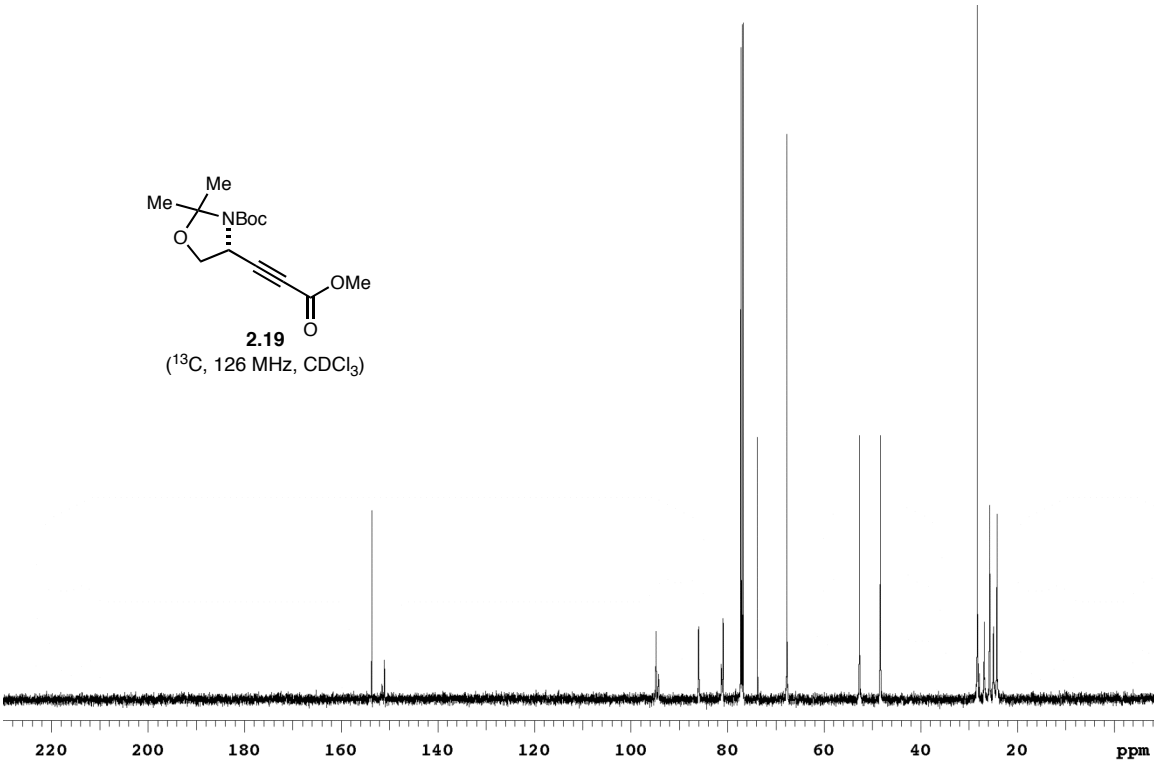

**2.9**
($^{1}$H, 500 MHz, $CDCl_3$)



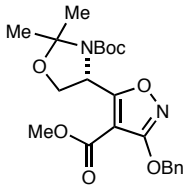

**2.9**
($^{13}$C, 126 MHz, $CDCl_3$)




**2.19**
($^{1}$H, 500 MHz, $CDCl_3$)

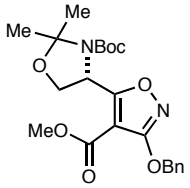



**2.19**
($^{13}$C, 126 MHz, $CDCl_3$)

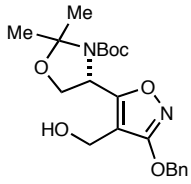



**2.20**
($^1$H, 500 MHz, $CDCl_3$)



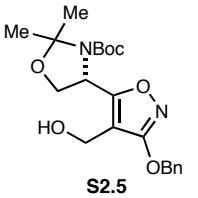




**2.20**
($^{13}$C, 126 MHz, $CDCl_3$)




**S2.5**
($^1$H, 500 MHz, $CDCl_3$)

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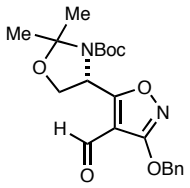
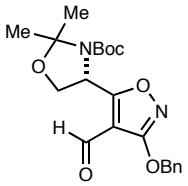
($^{13}$C, 126 MHz, $CDCl_3$)

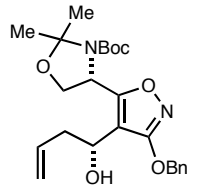



**S2.6**
($^{1}$H, 500 MHz, $CDCl_3$)



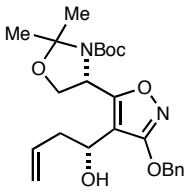

**S2.6**
($^{13}$C, 126 MHz, $CDCl_3$)




**2.21**

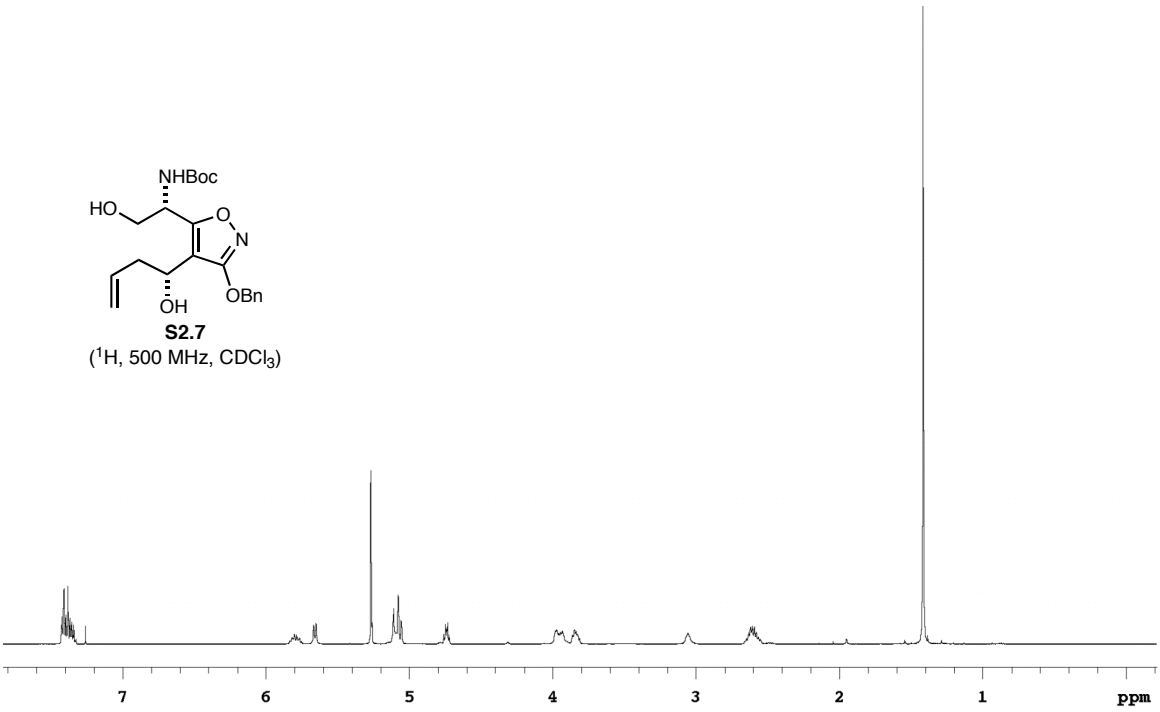
($^{1}$H, 500 MHz, $CDCl_3$)



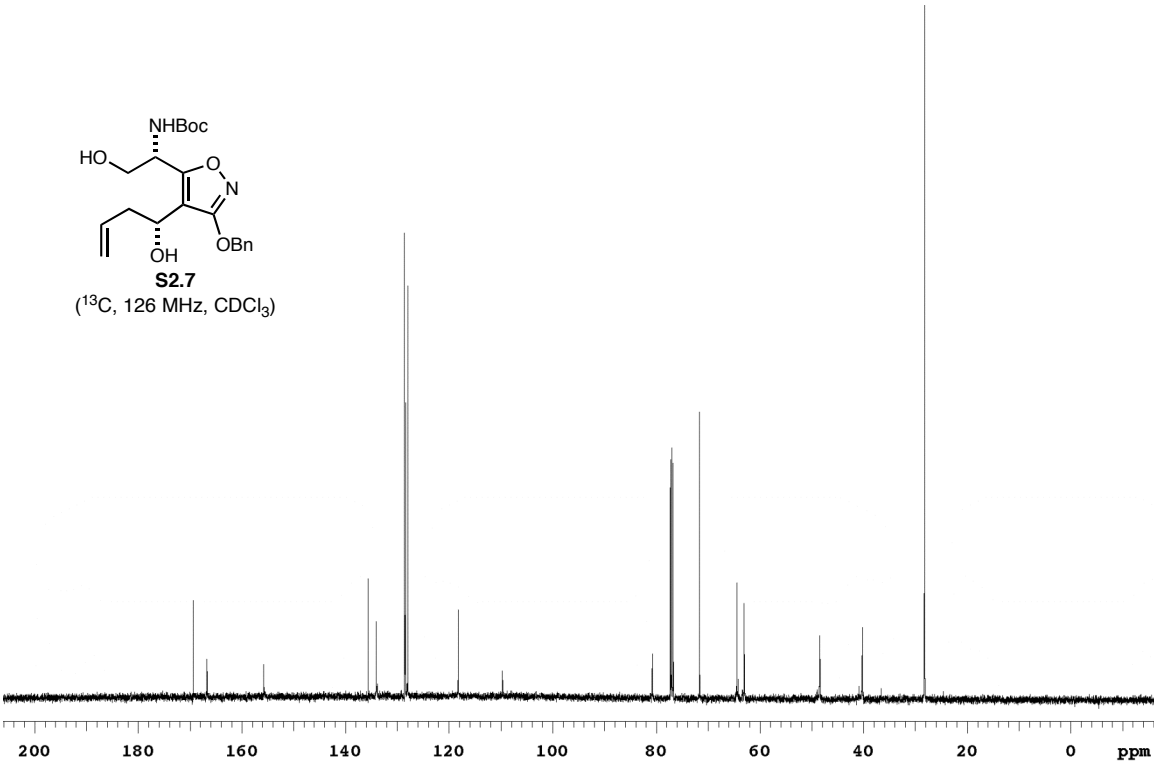




**2.21**

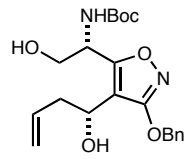
($^{13}$C, 126 MHz, $CDCl_3$)



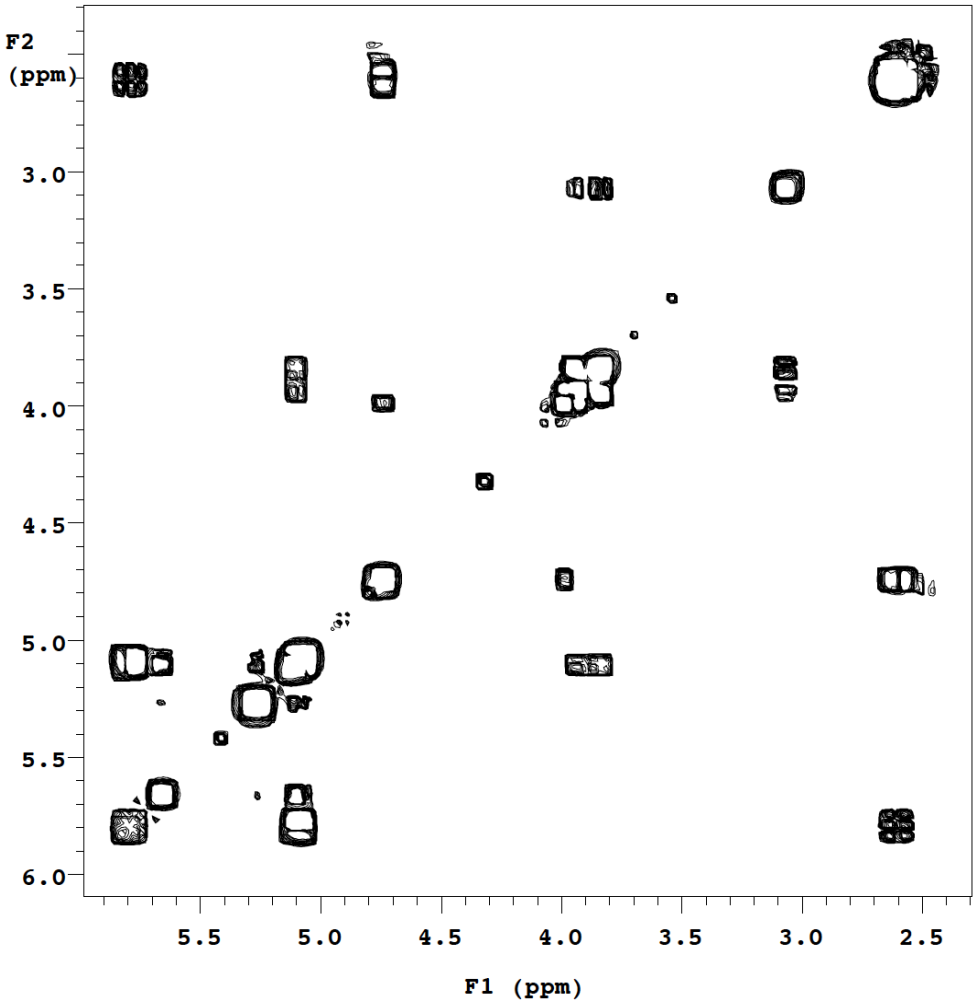

**S2.7**
($^1$H, 500 MHz, $CDCl_3$)

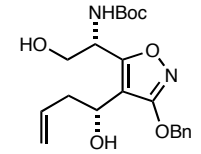



**S2.7**
($^{13}$C, 126 MHz, $CDCl_3$)

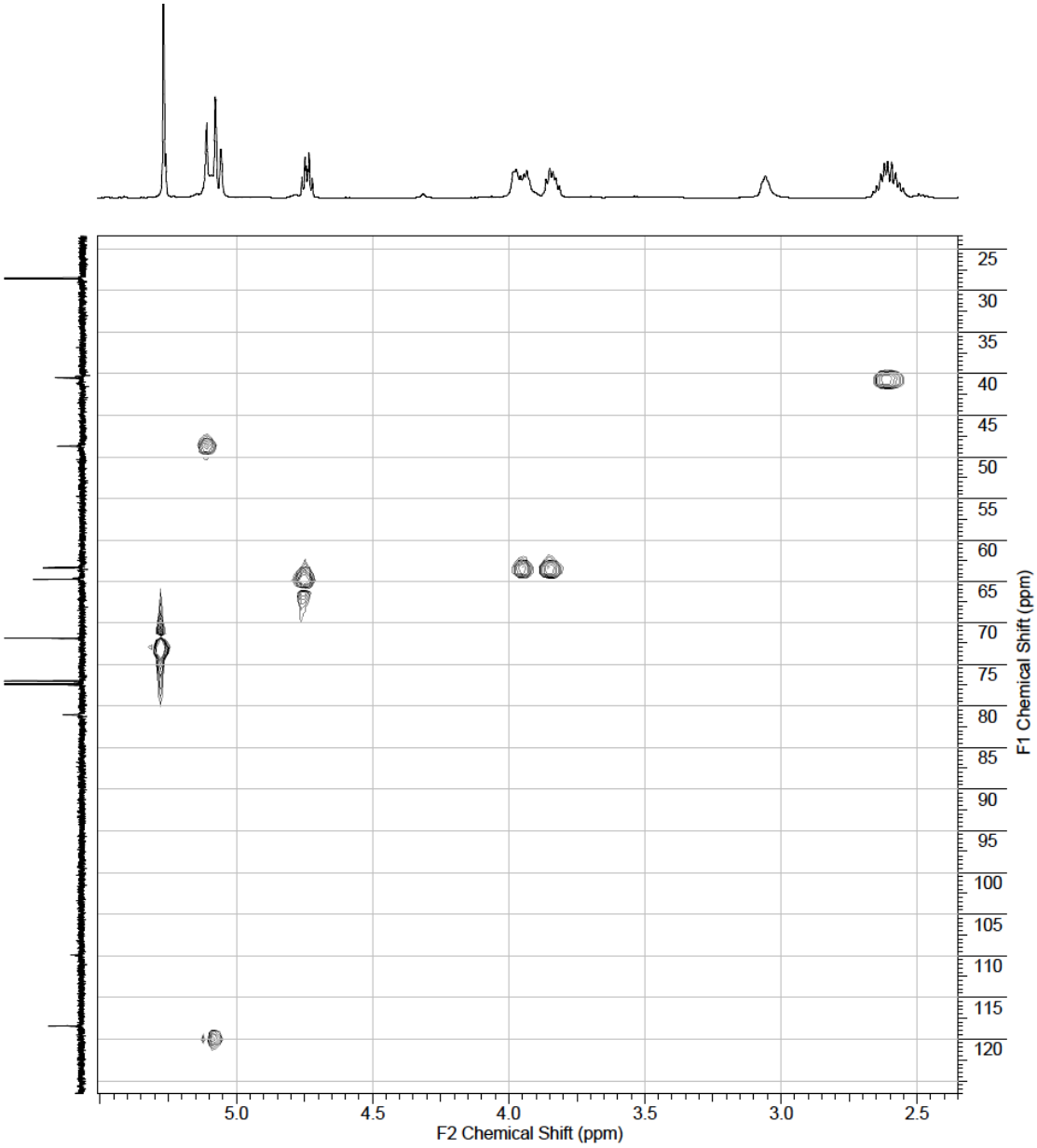


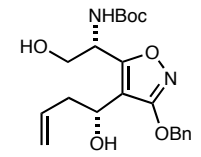

**S2.7**
(COSY, 500 MHz, $CDCl_3$)



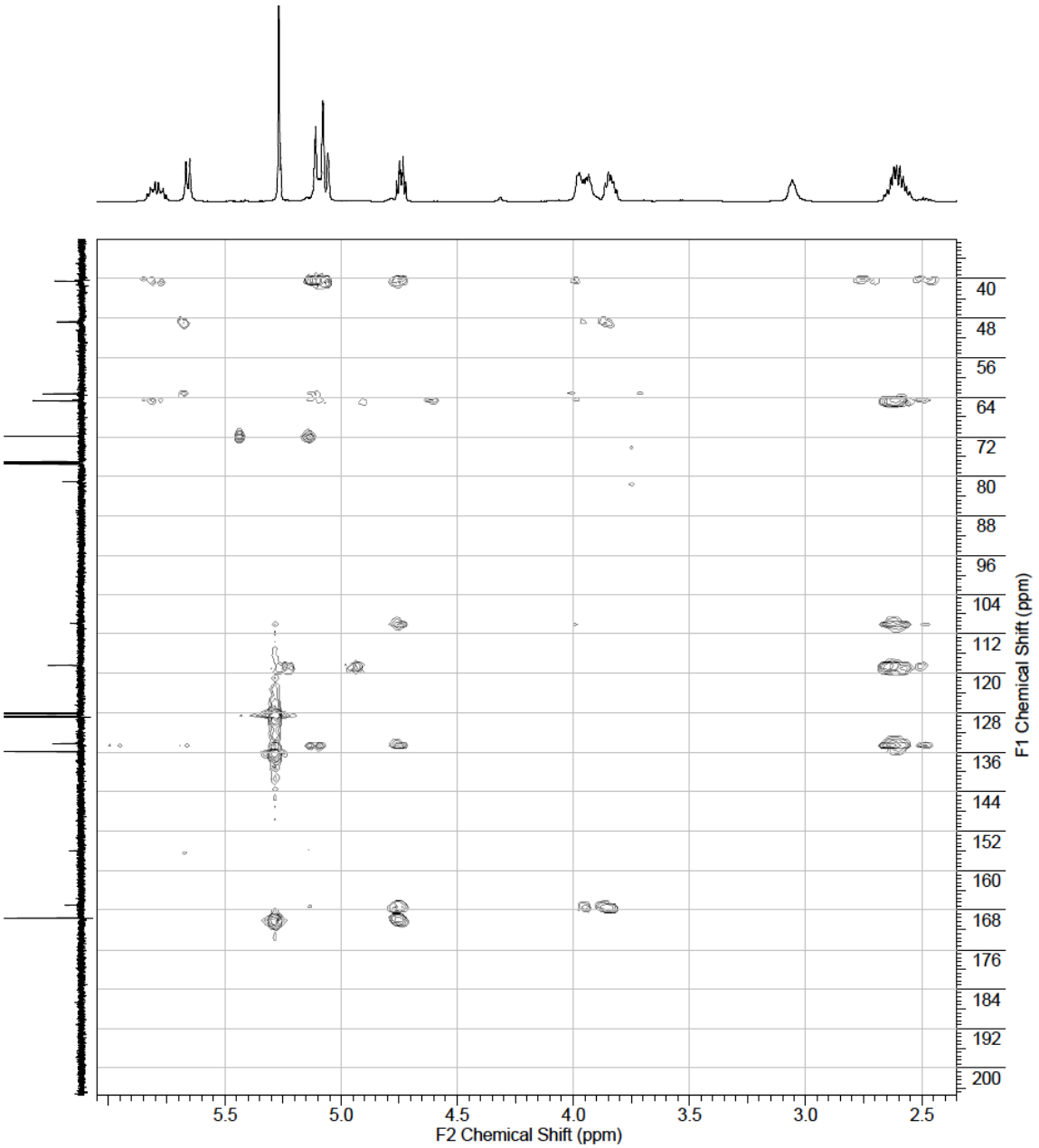


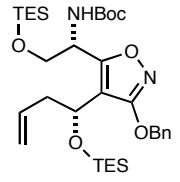

**S2.7**
(HSQC, 500 MHz, $CDCl_3$)






**S2.7**
(HMBC, 500 MHz, $CDCl_3$)

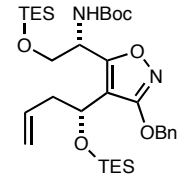





**S2.8**

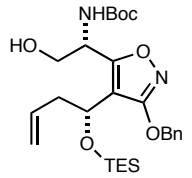
($^1$H, 500 MHz, $CDCl_3$)



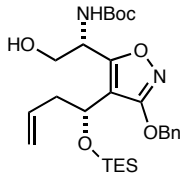

**S2.8**

($^{13}$C, 126 MHz, $CDCl_3$)

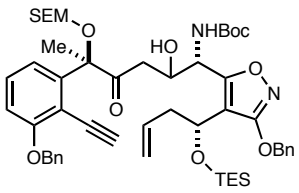



**2.22**
($^1$H, 500 MHz, $CDCl_3$)



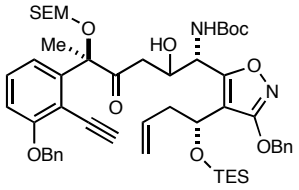




**2.22**
($^{13}$C, 126 MHz, $CDCl_3$)

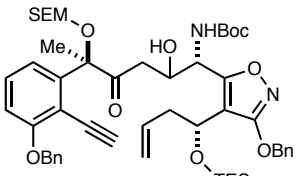



**S2.9a** diastereomer #1
(higher Rf)
($^{1}$H, 500 MHz, $CDCl_3$)



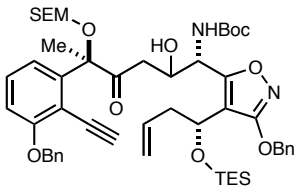




**S2.9a** diastereomer #1
(higher Rf)
($^{13}$C, 126 MHz, $CDCl_3$)

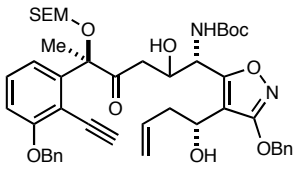



**S2.9b** diastereomer #2
(Lower Rf)
($^1$H, 500 MHz, $CDCl_3$)



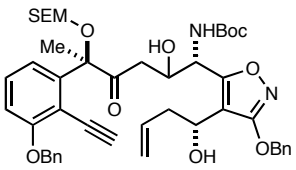




**S2.9b** diastereomer #2
(Lower Rf)
($^{13}$C, 126 MHz, $CDCl_3$)

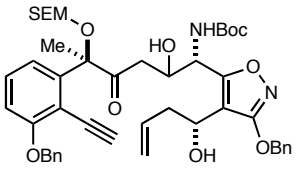



**2.35a** diastereomer #1
(higher Rf)
($^1$H, 500 MHz, $CDCl_3$)



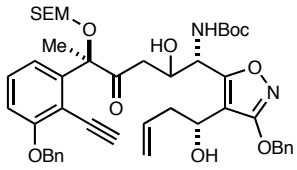




**2.35a** diastereomer #1
(higher Rf)
($^{13}$C, 126 MHz, $CDCl_3$)

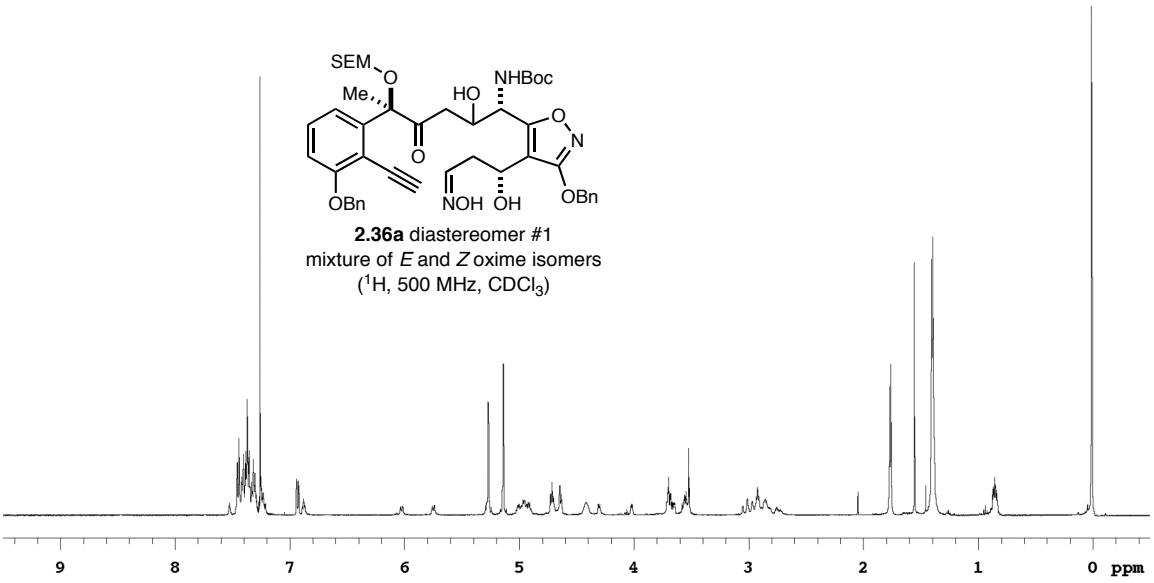



**2.35b** diastereomer #2
(lower Rf)
($^1$H, 500 MHz, $CDCl_3$)

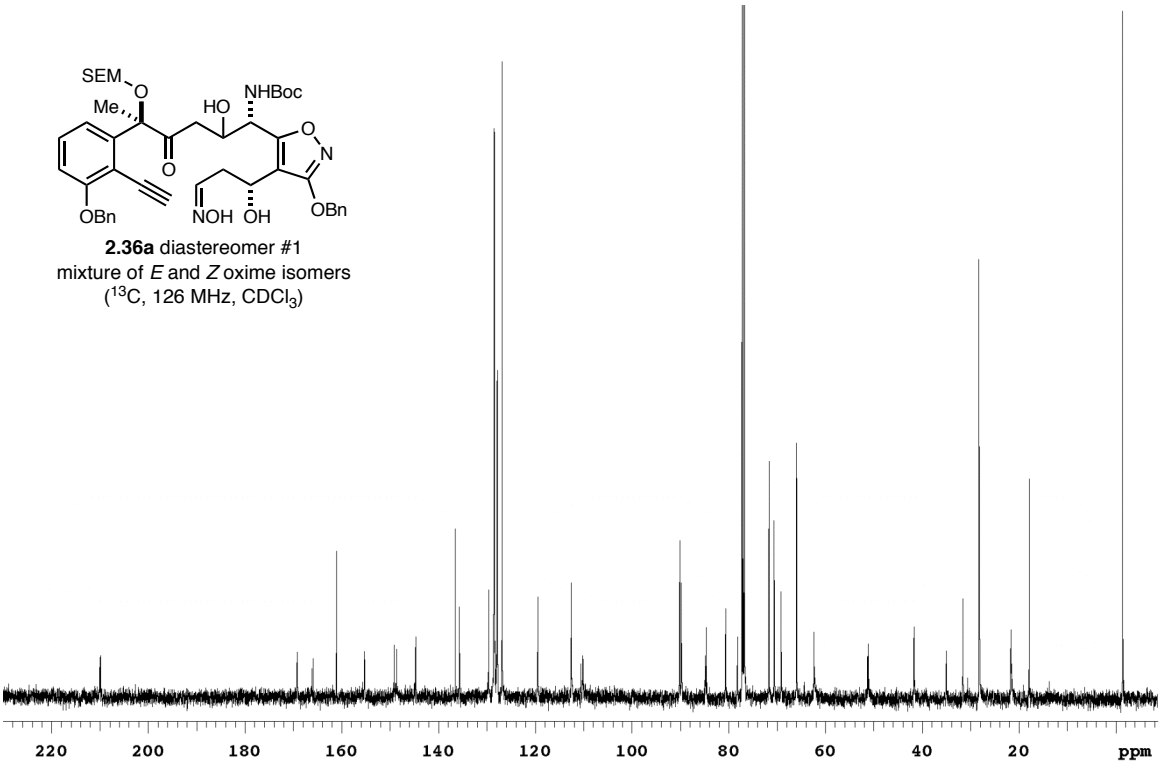


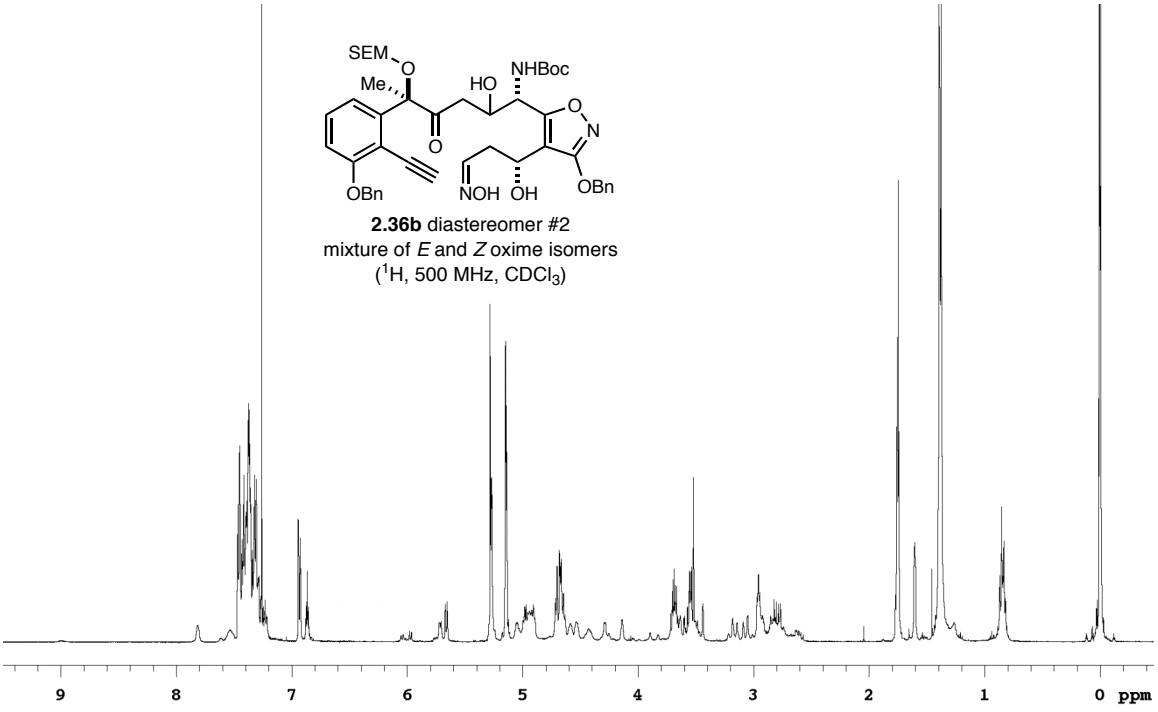

**2.35b** diastereomer #2
(lower Rf)
($^{13}$C, 126 MHz, $CDCl_3$)



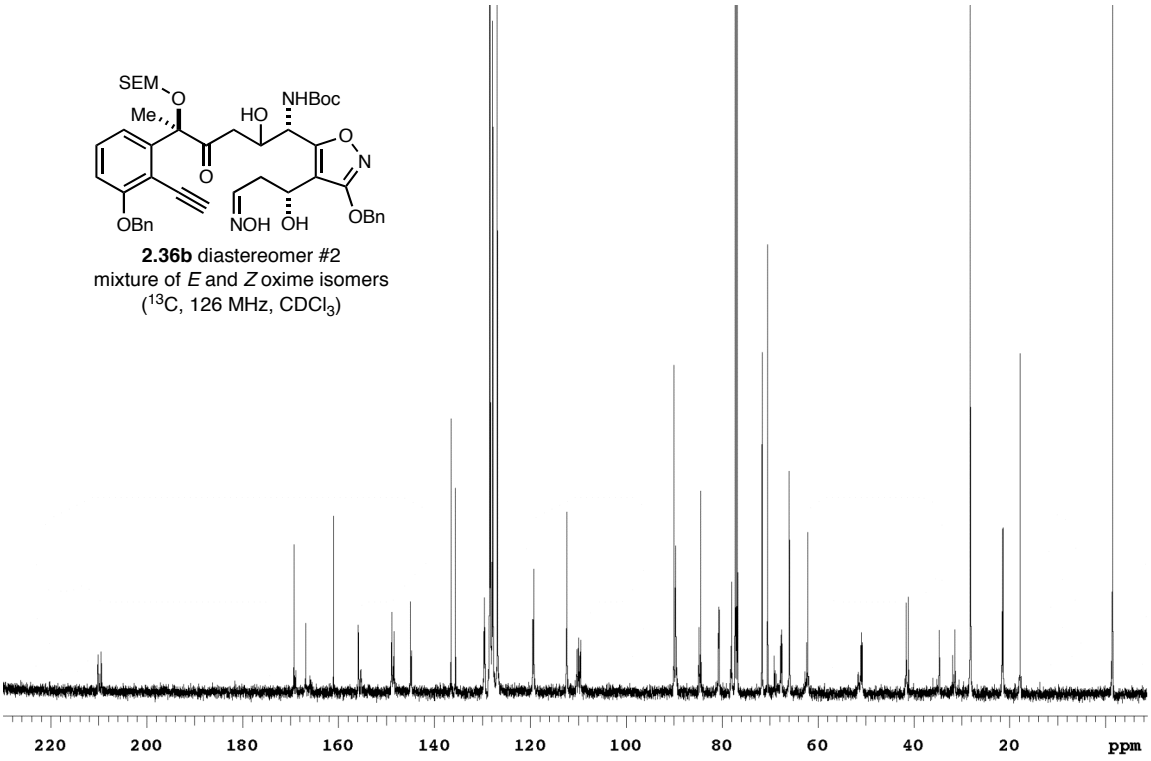

**2.36a** diastereomer #1
mixture of *E* and *Z* oxime isomers
($^{1}$H, 500 MHz, $CDCl_3$)



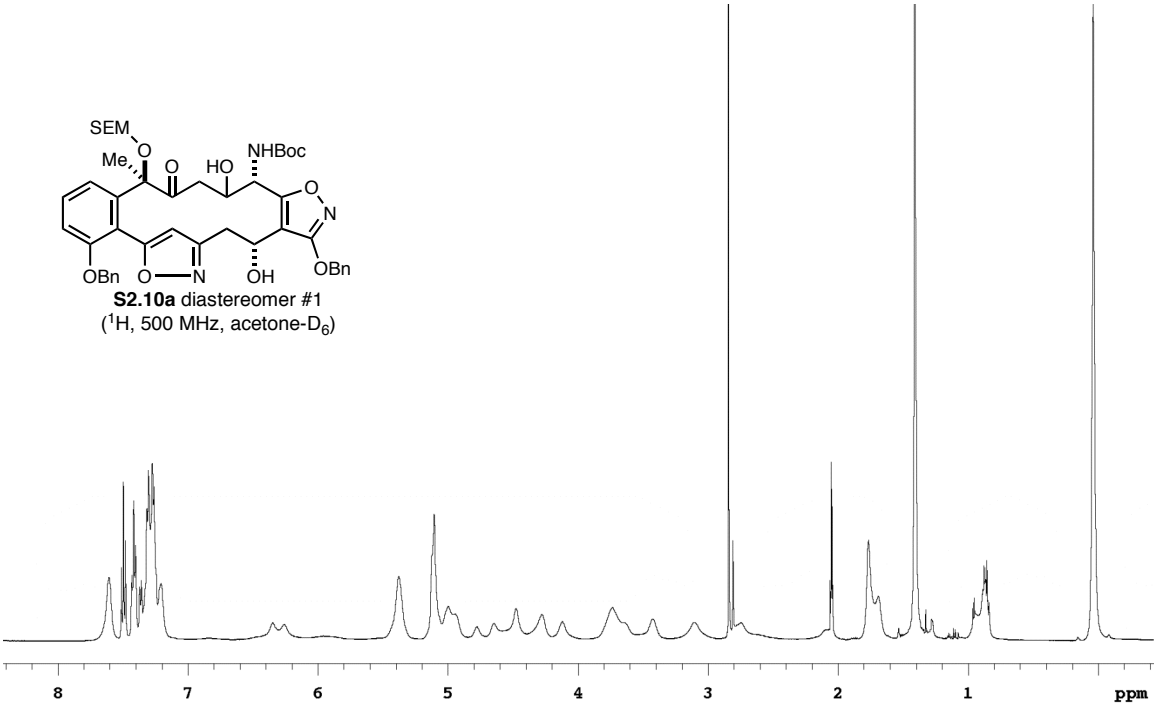

**2.36a** diastereomer #1
mixture of *E* and *Z* oxime isomers
($^{13}$C, 126 MHz, $CDCl_3$)



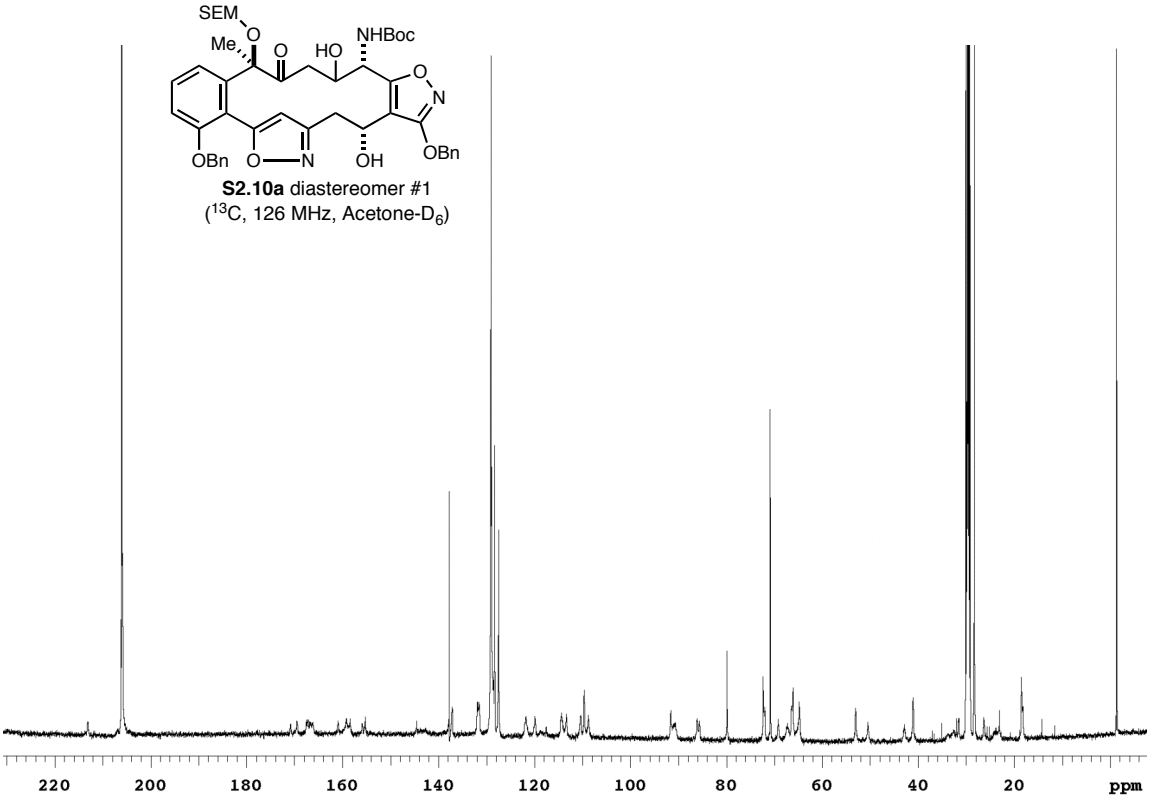

**2.36b** diastereomer #2
mixture of *E* and *Z* oxime isomers
($^{1}$H, 500 MHz, $CDCl_3$)



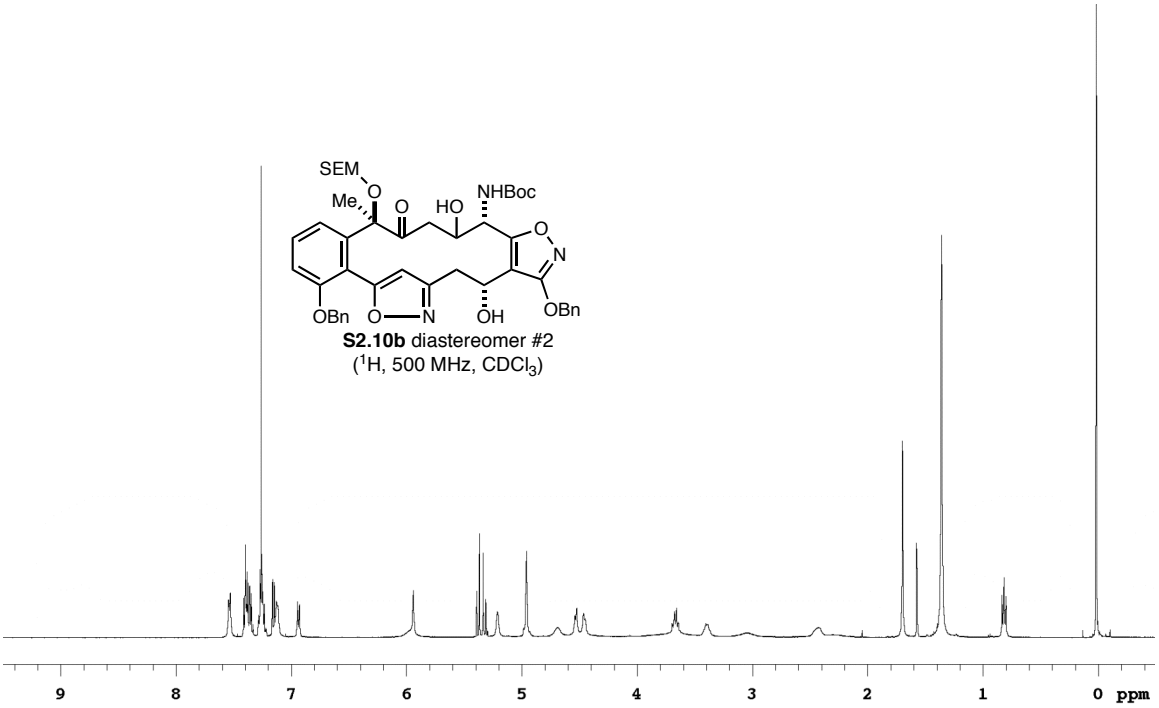

**2.36b** diastereomer #2
mixture of *E* and *Z* oxime isomers
($^{13}$C, 126 MHz, $CDCl_3$)



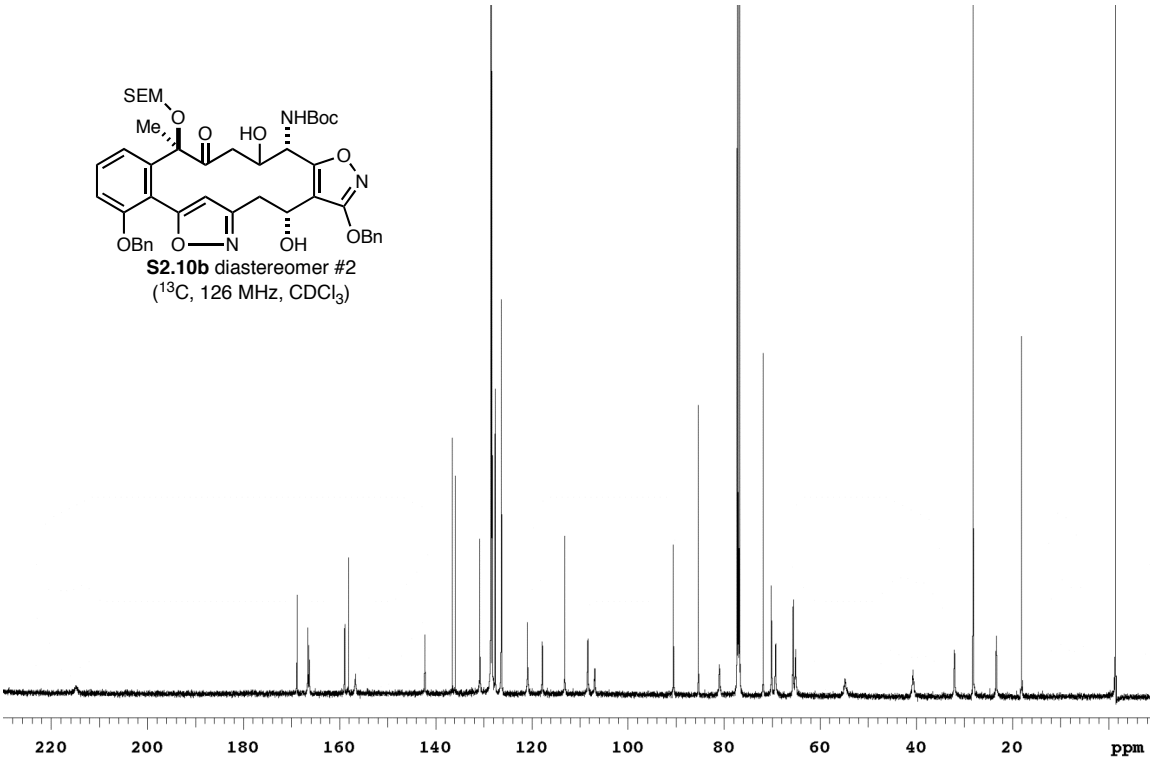

**S2.10a** diastereomer #1
($^1$H, 500 MHz, acetone-$D_6$)



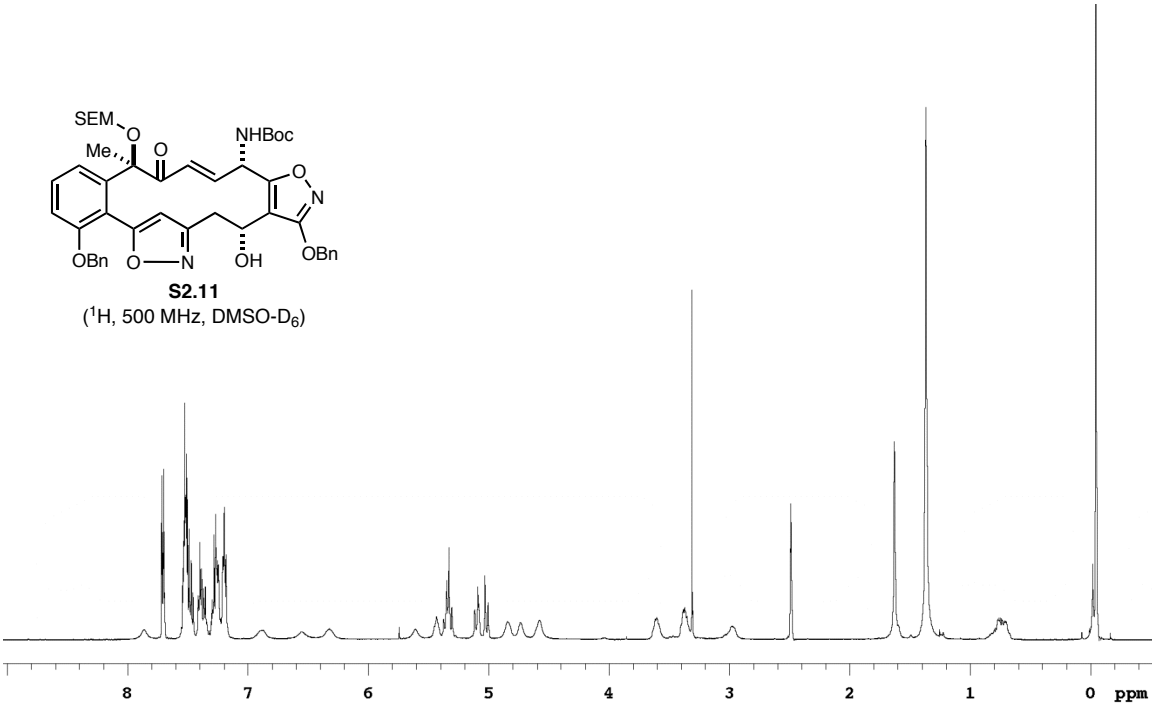

**S2.10a** diastereomer #1
($^{13}$C, 126 MHz, Acetone-$D_6$)



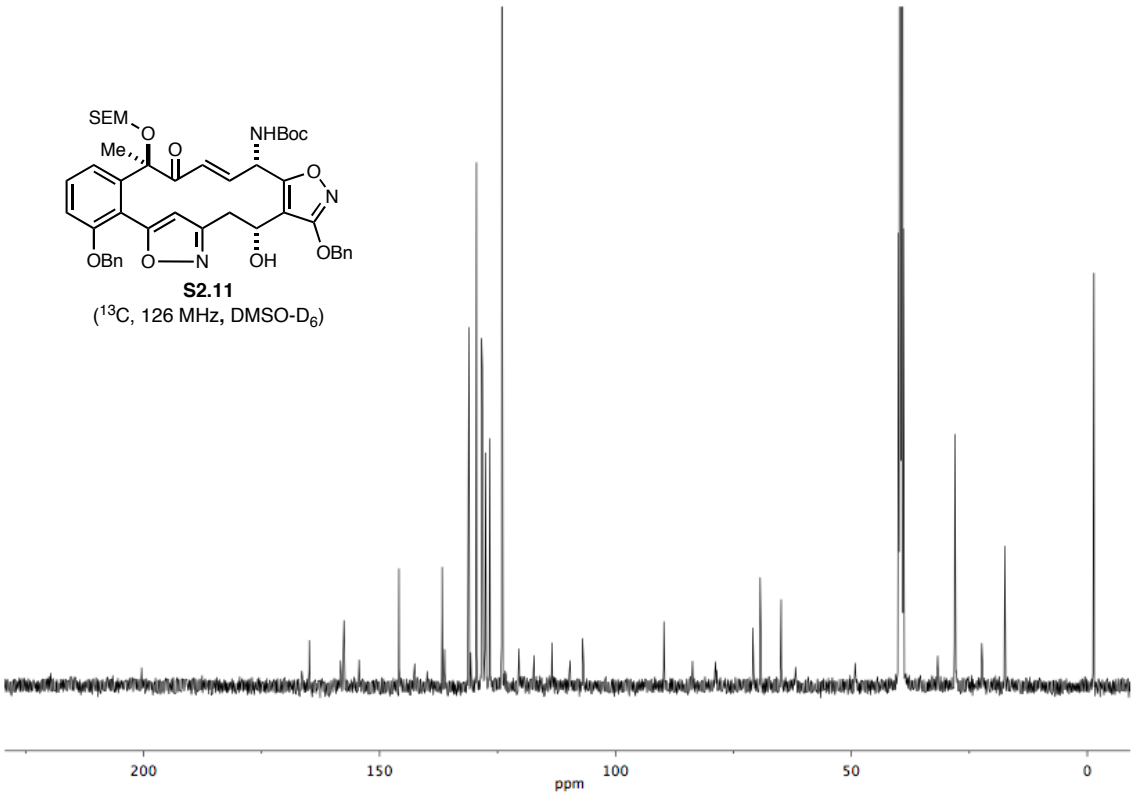

**S2.10b** diastereomer #2
($^{1}$H, 500 MHz, $CDCl_3$)



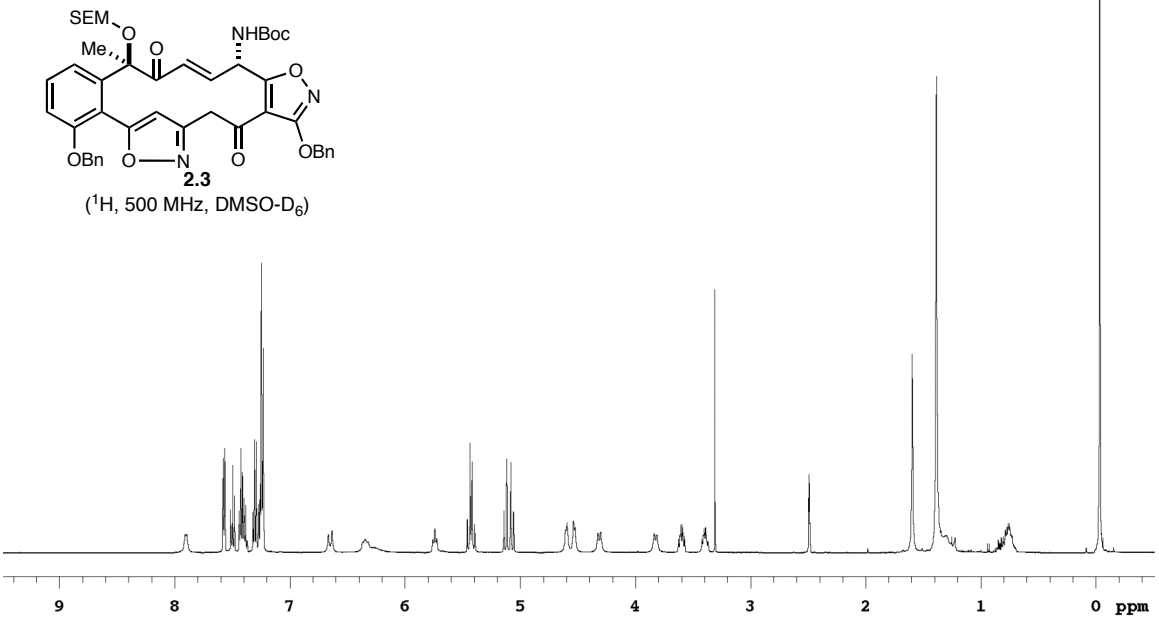

**S2.10b** diastereomer #2
($^{13}$C, 126 MHz, $CDCl_3$)




**S2.11**
($^{1}$H, 500 MHz, DMSO-$D_6$)

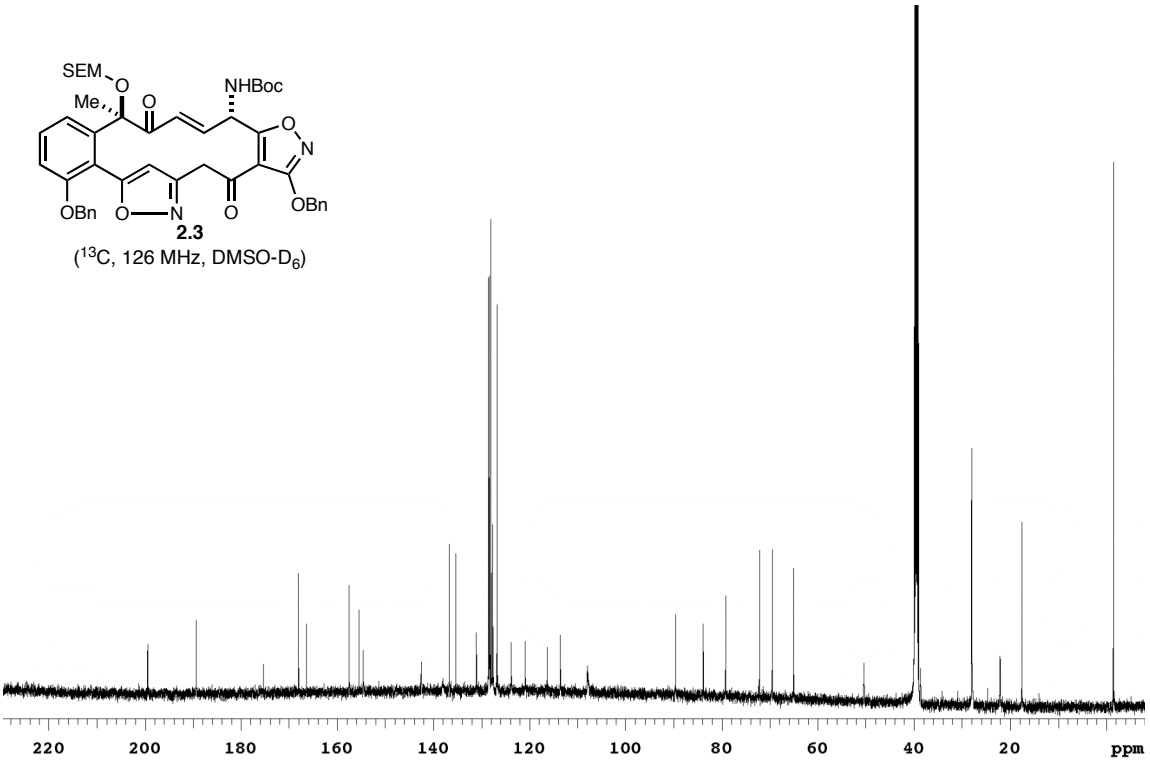



**S2.11**
($^{13}$C, 126 MHz, DMSO-$D_6$)



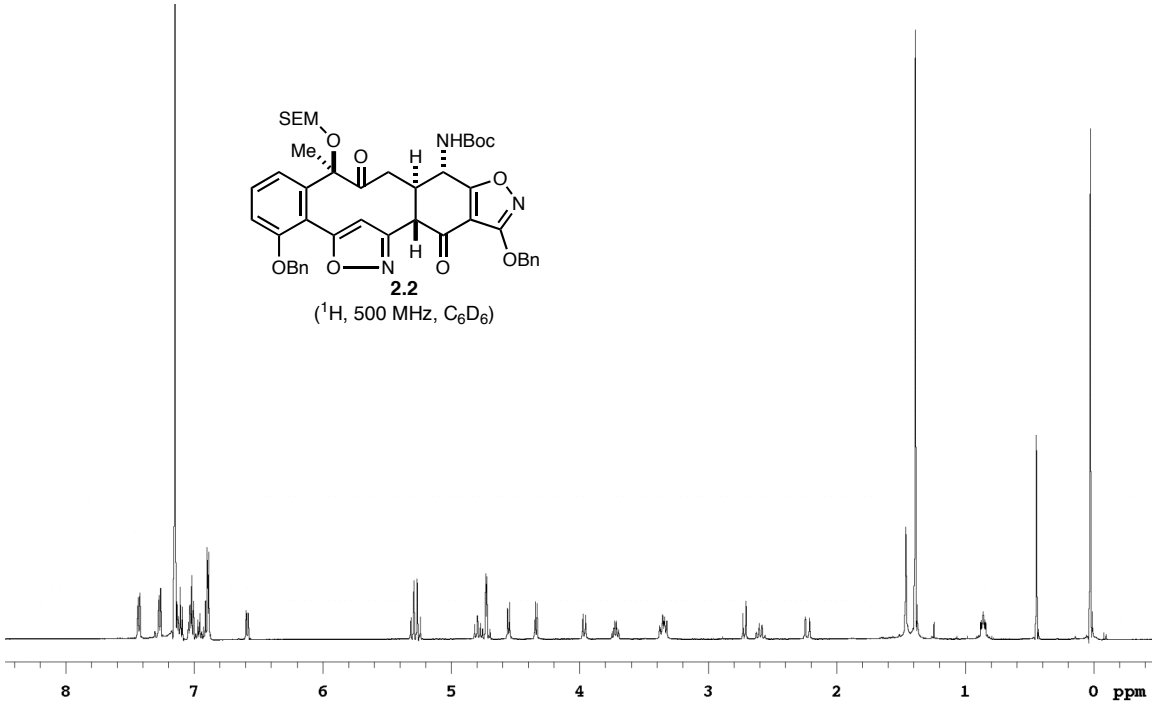

**2.3**

($^{1}$H, 500 MHz, DMSO-$D_6$)



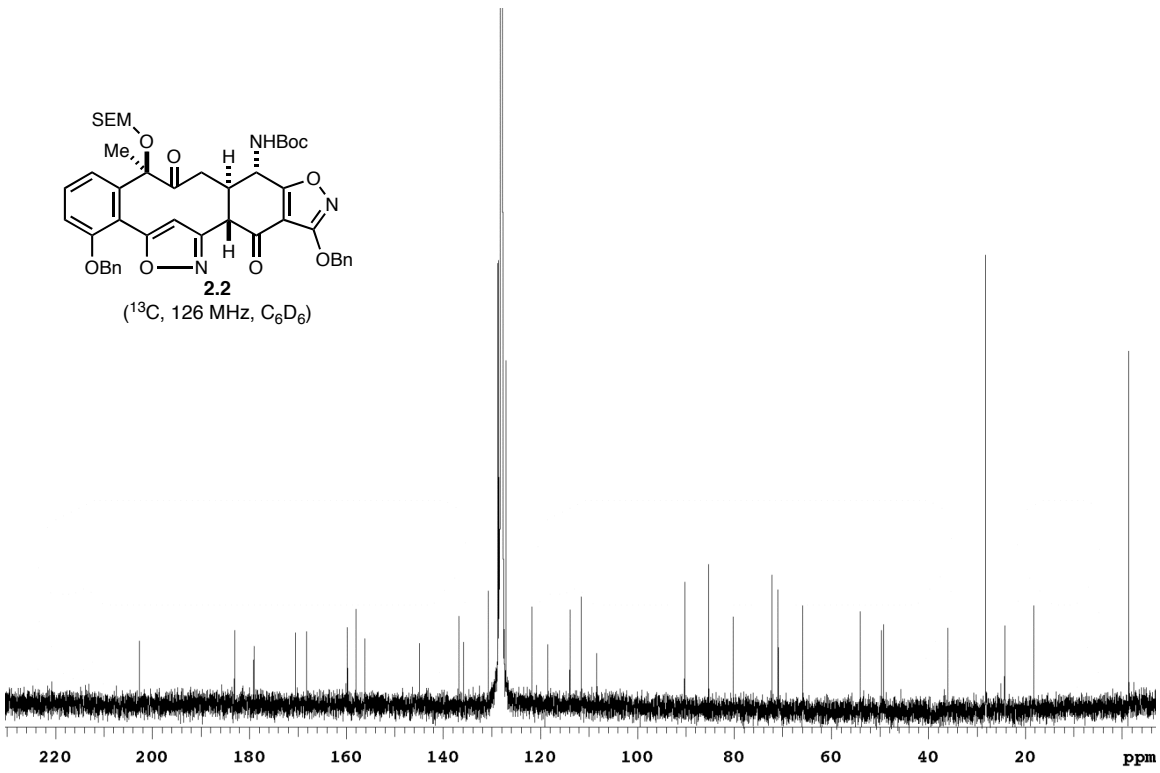

**2.3**

($^{13}$C, 126 MHz, DMSO-$D_6$)



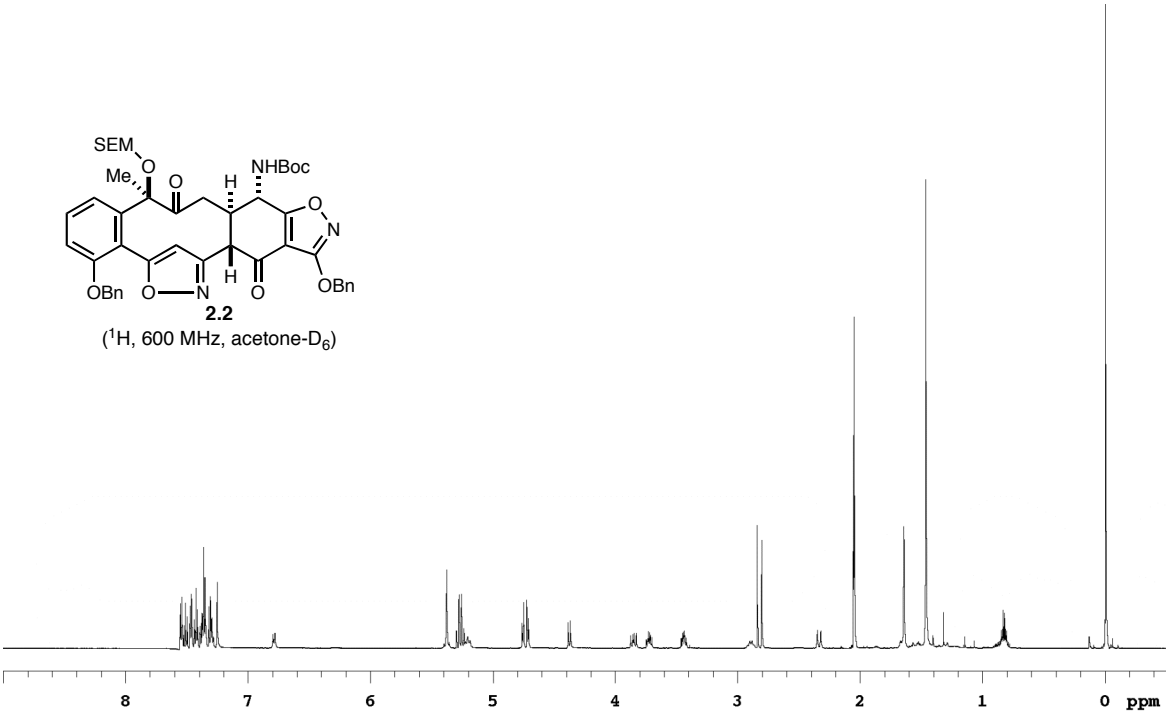

**2.2**

($^1$H, 500 MHz, $C_6D_6$)



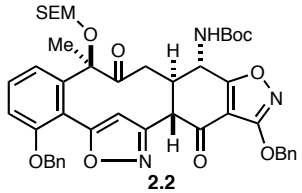

**2.2**

($^{13}$C, 126 MHz, $C_6D_6$)



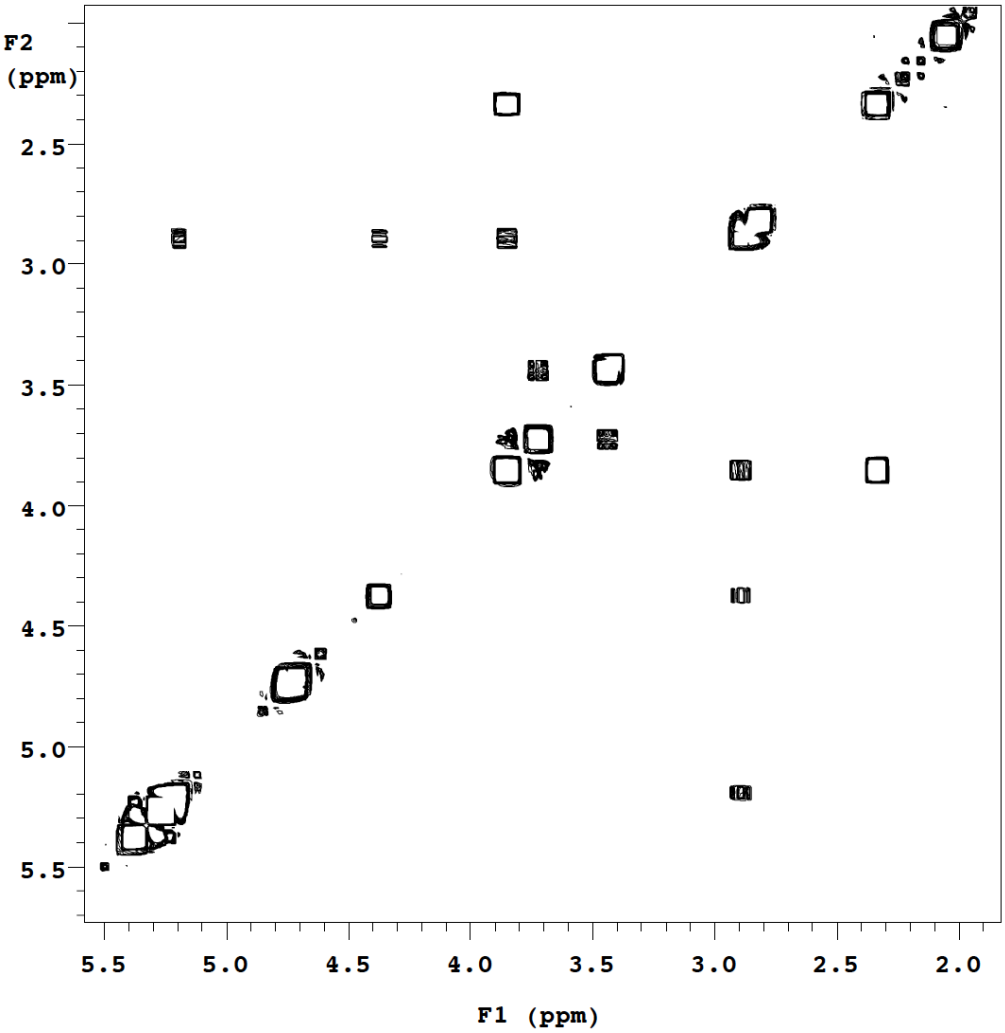

**2.2**

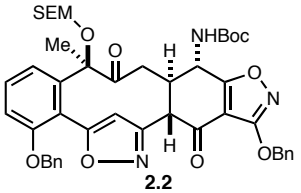
($^1$H, 600 MHz, acetone-$D_6$)




**2.2**

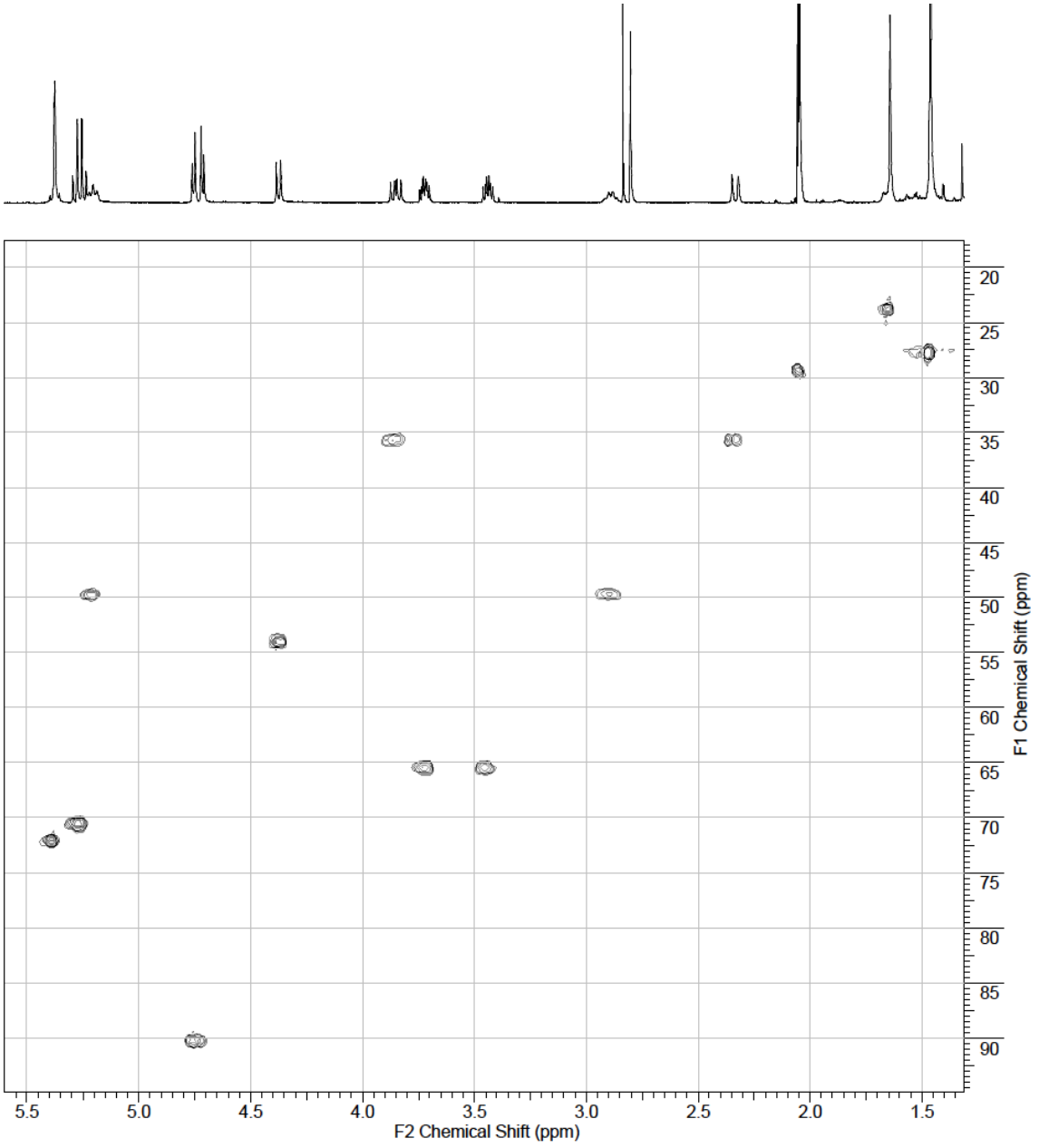
(COSY, 600 MHz, acetone-$D_6$)

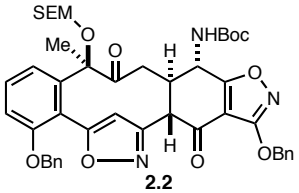





**2.2**

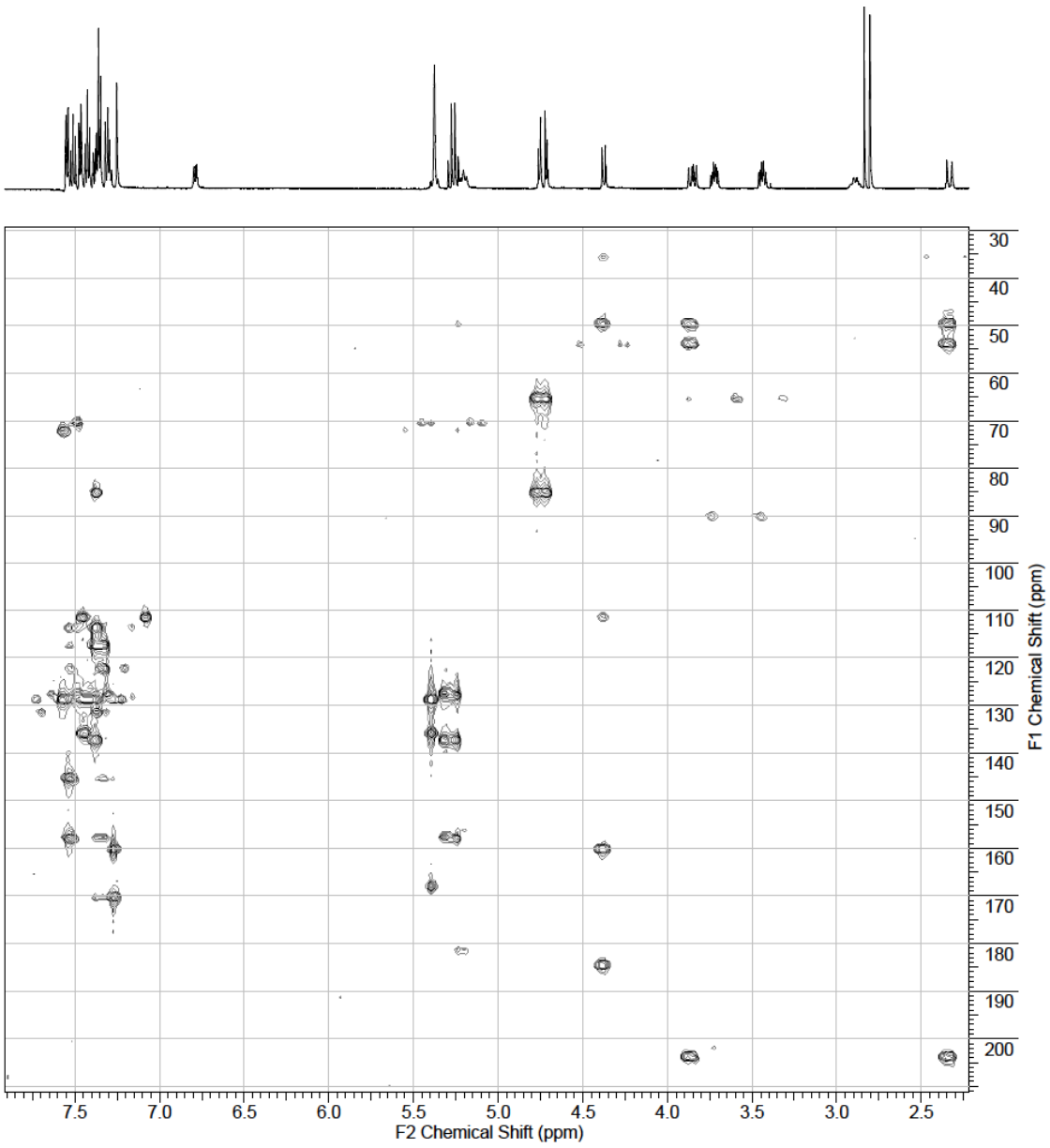
(HSQC, 500 MHz, acetone-$D_6$)

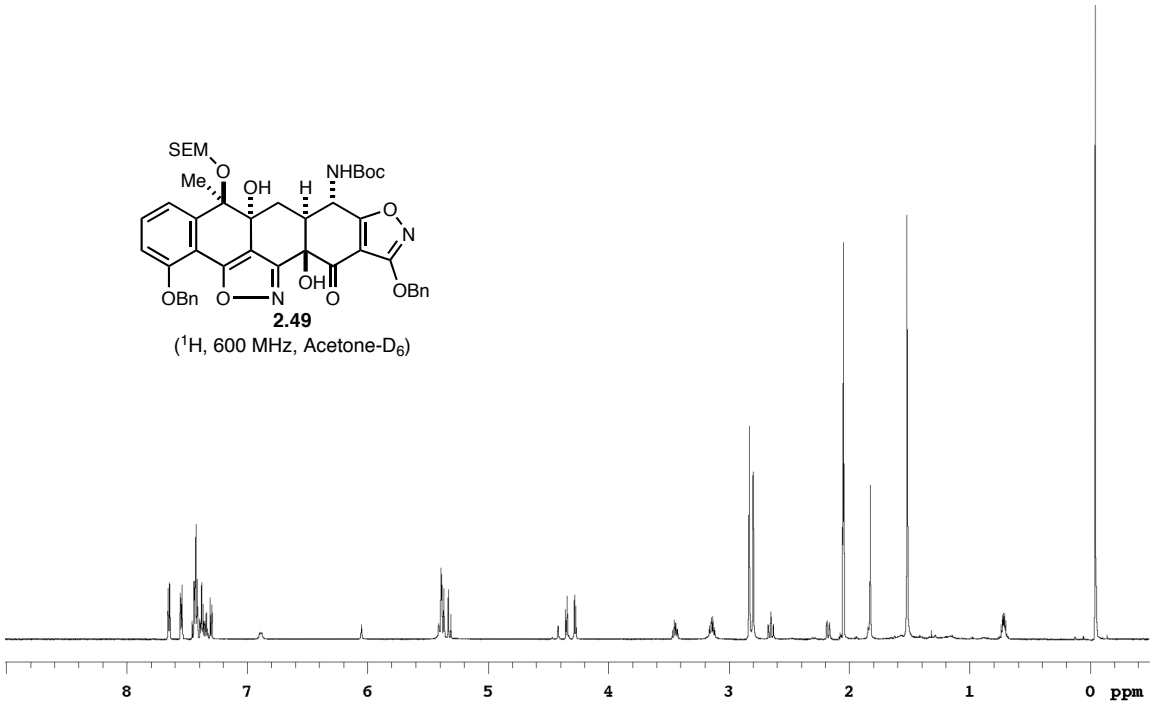





**2.2**

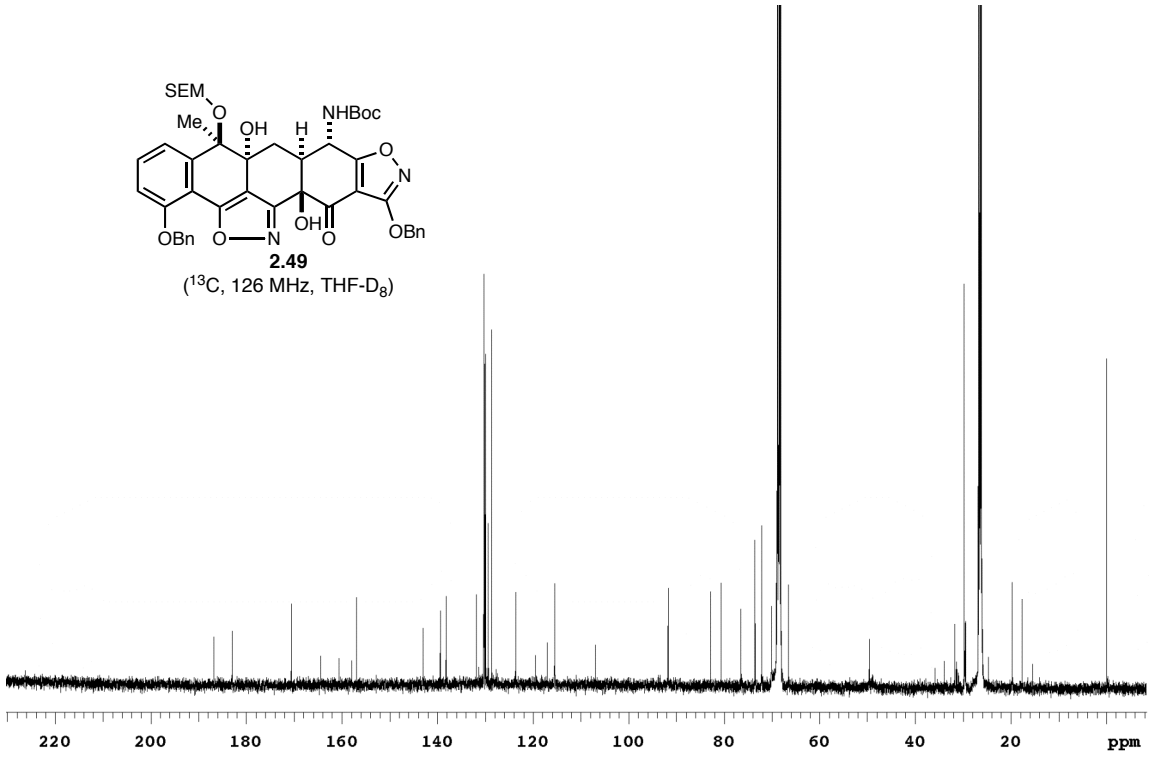
(HMBC, 500 MHz, acetone-$D_6$)





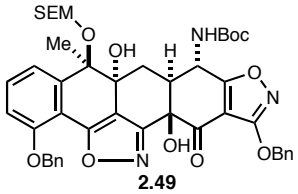

**2.49**

($^{1}$H, 600 MHz, Acetone-$D_6$)



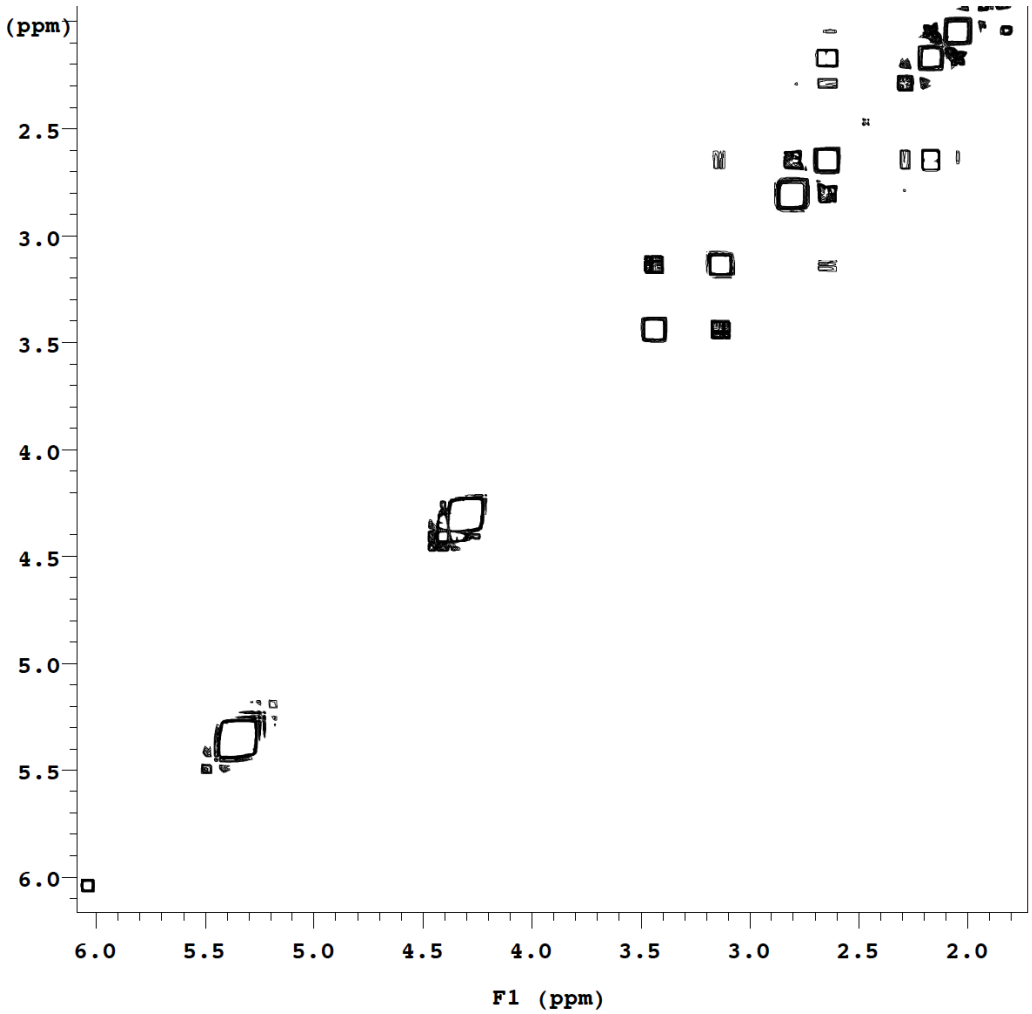

**2.49**

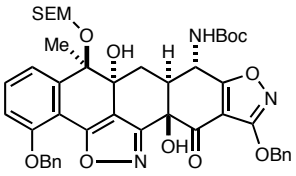
($^{13}$C, 126 MHz, THF-$D_8$)




**2.49**

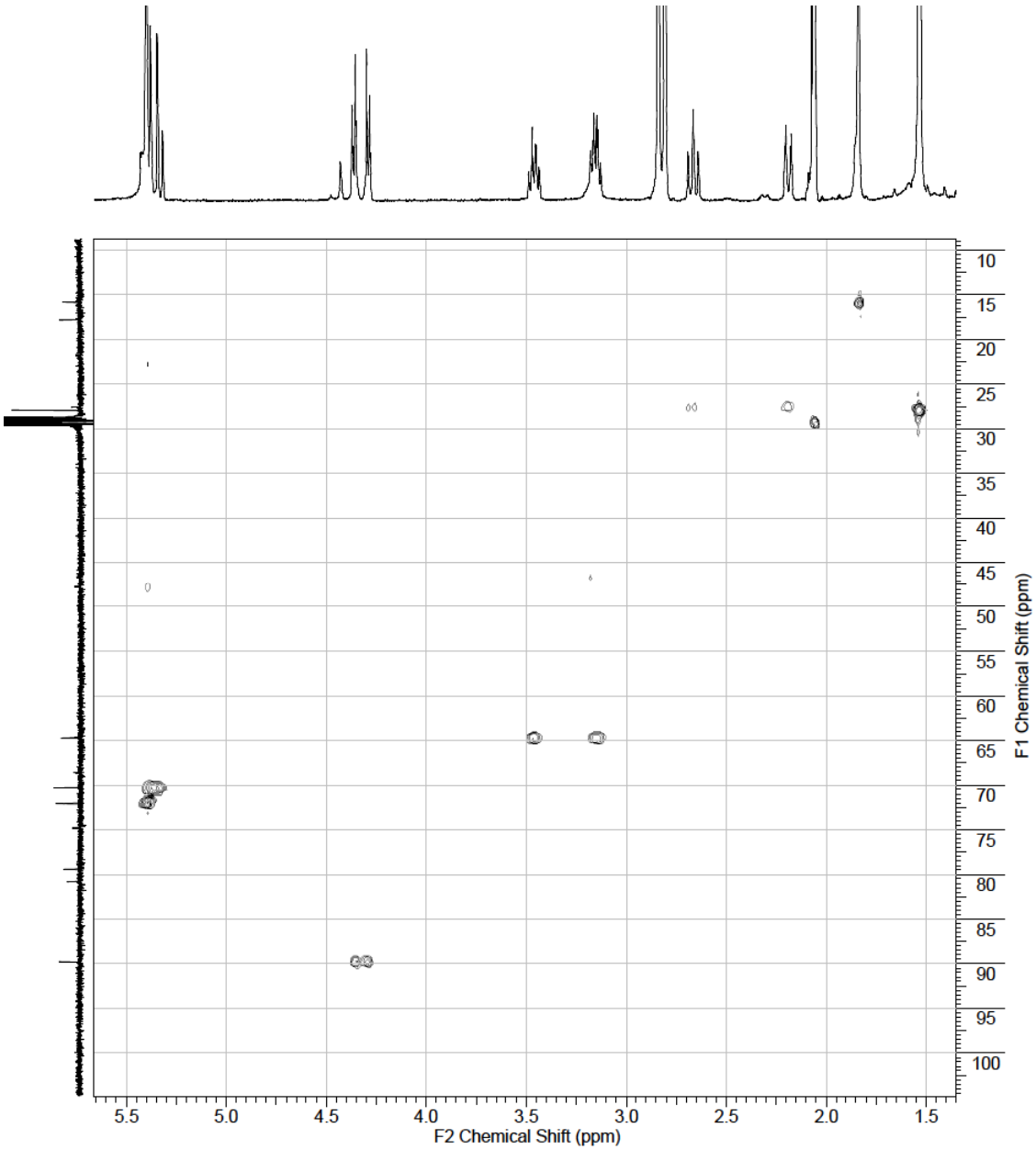
(COSY, 600 MHz, Acetone-$D_6$)

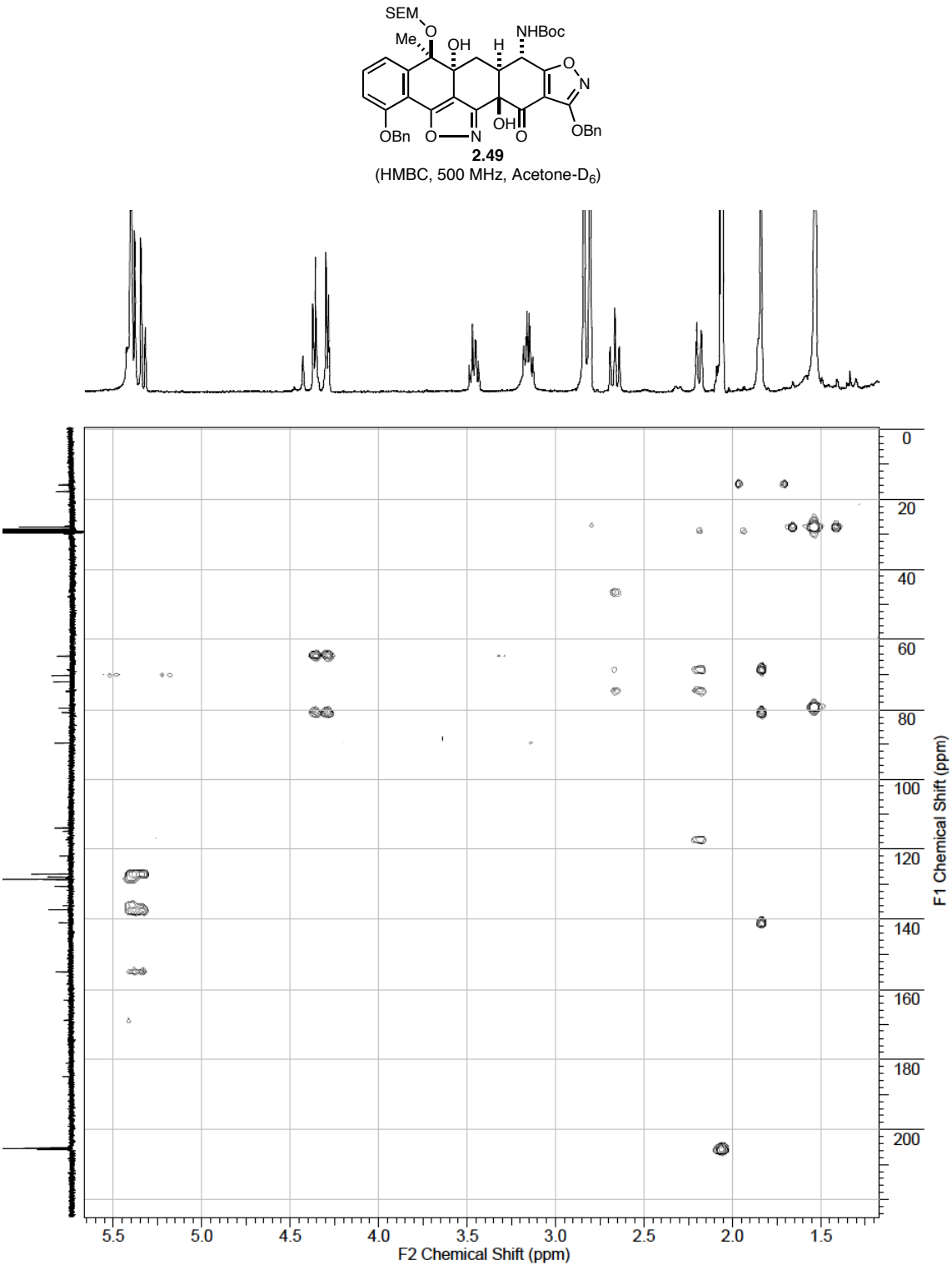





**2.49**

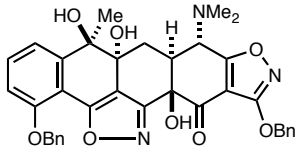
(HSQC, 500 MHz, Acetone-$D_6$)






**2.49**

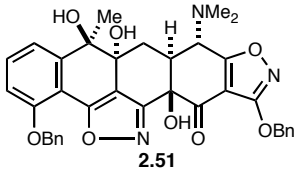
(HMBC, 500 MHz, Acetone-$D_6$)




**2.51**

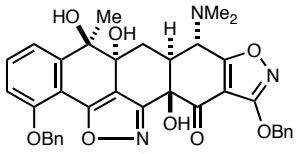
($^1$H, 500 MHz, THF-$D_8$)



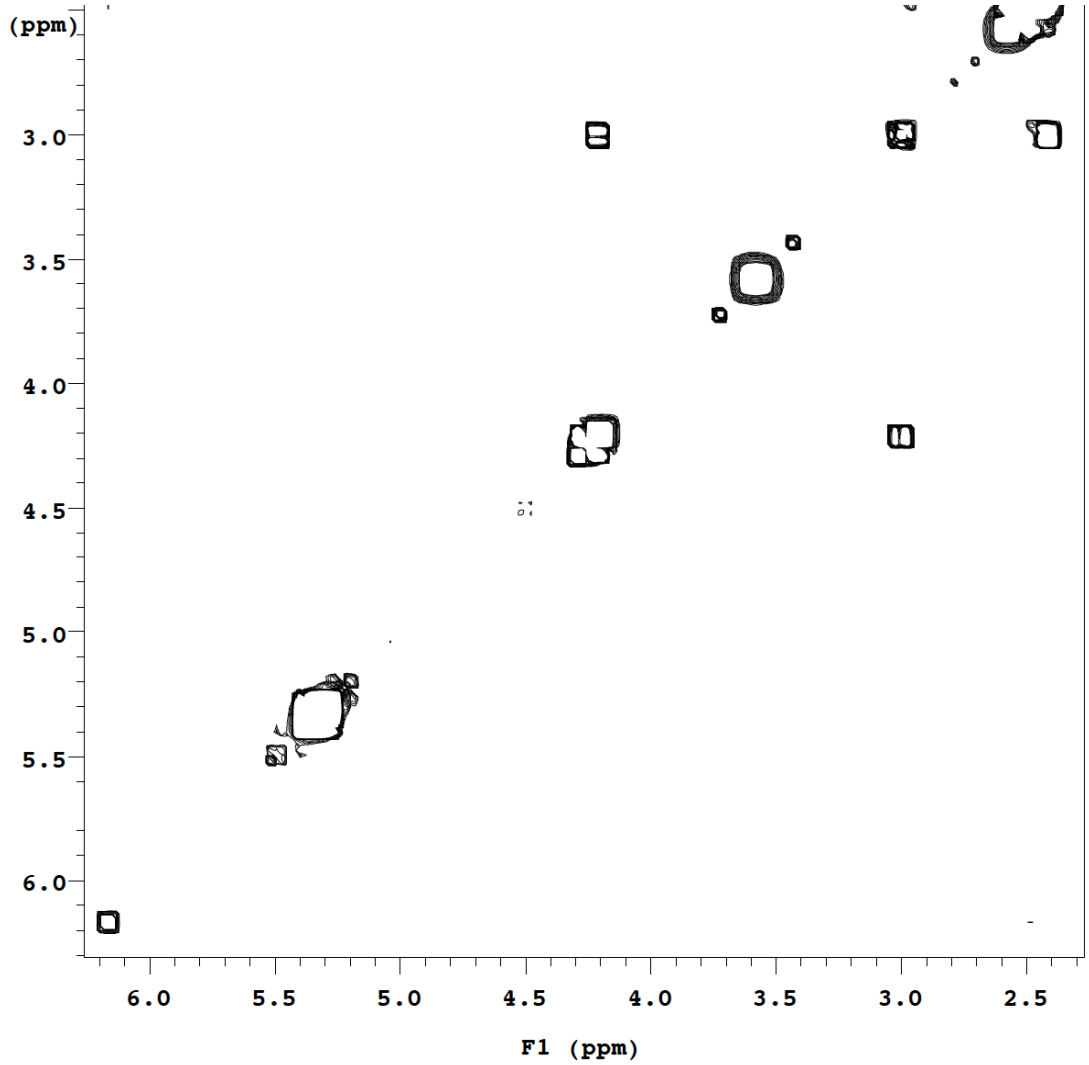

**2.51**

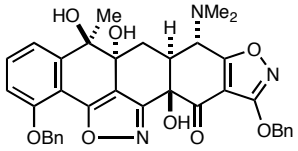
($^{13}$C, 126 MHz, THF-$D_8$)




**2.51**

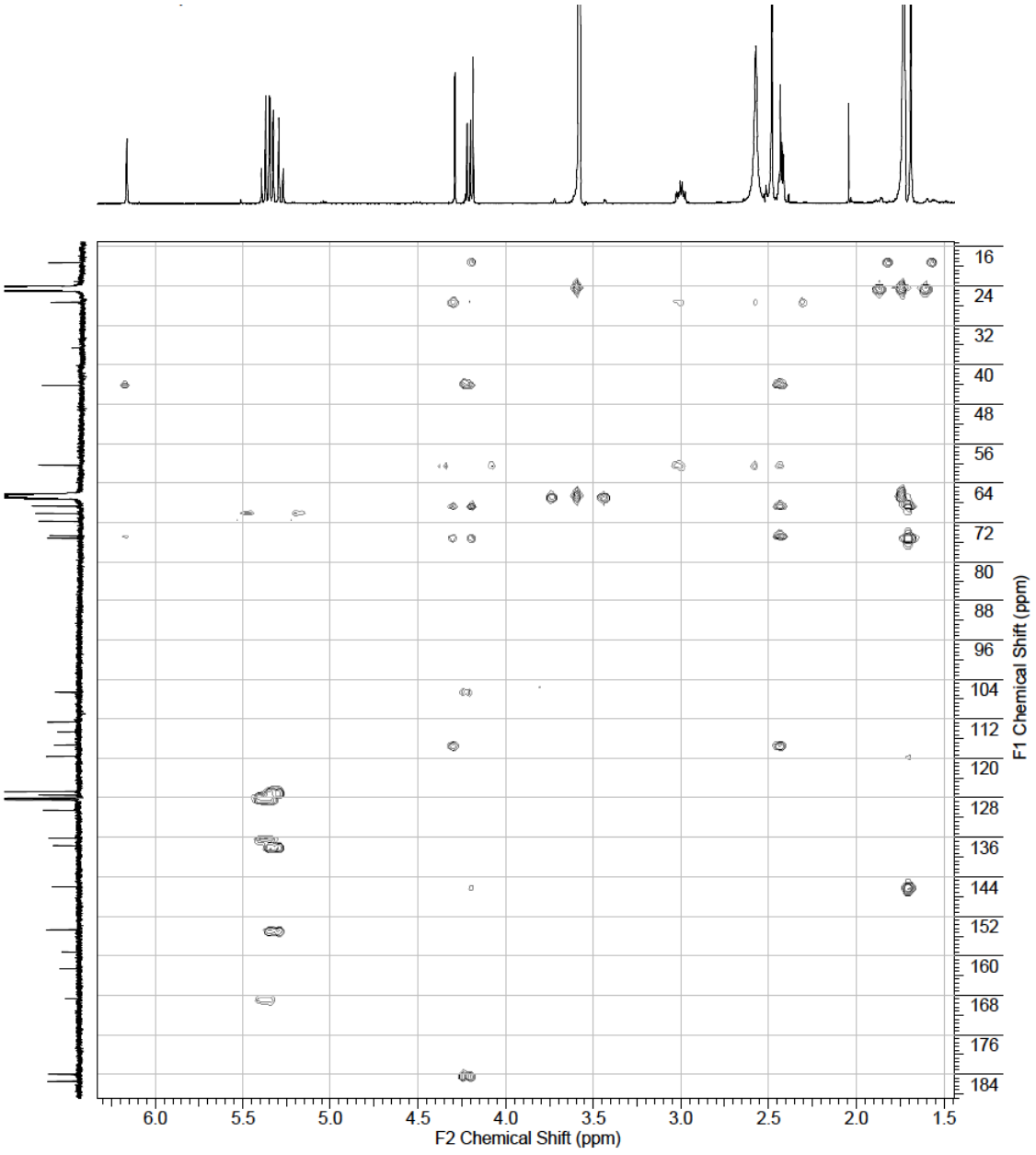
(COSY, 500 MHz, THF-$D_8$)

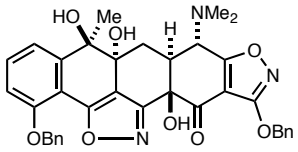





**2.51**

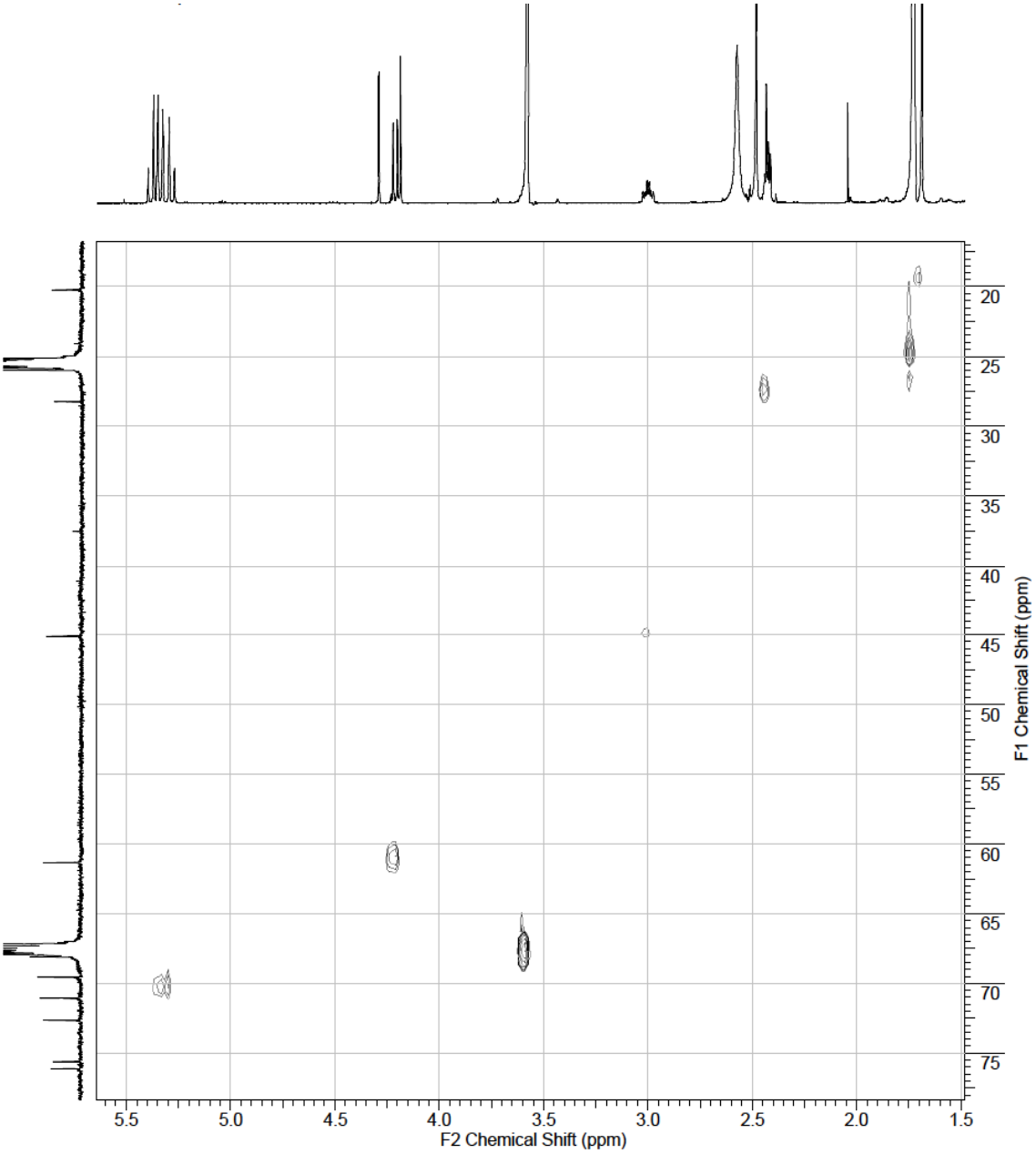
(HMBC, 500 MHz, THF-$D_8$)

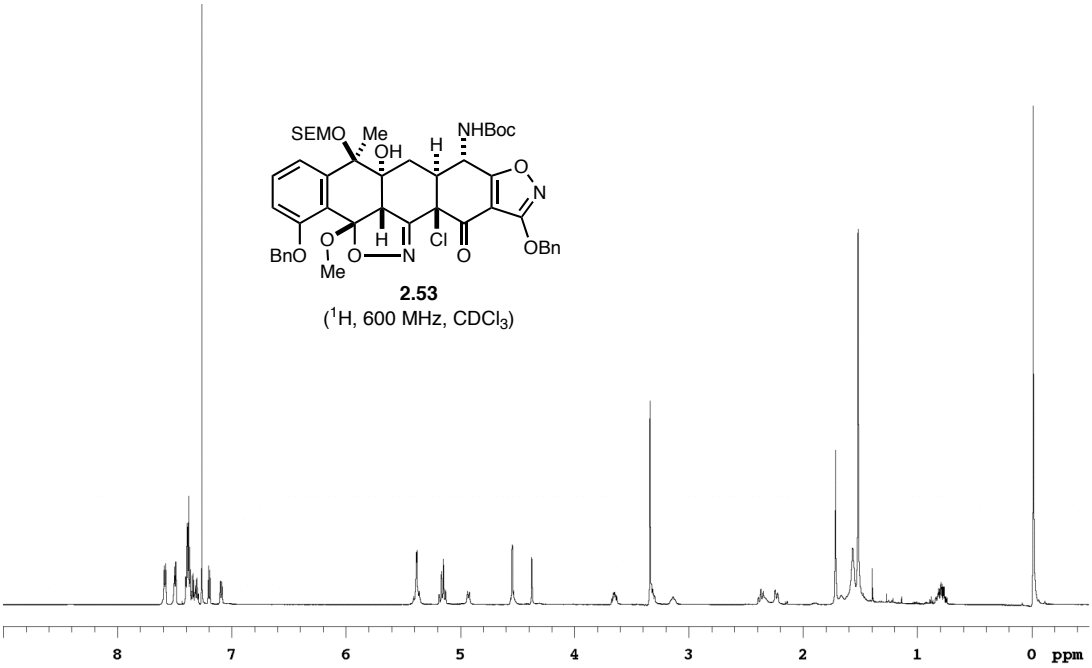




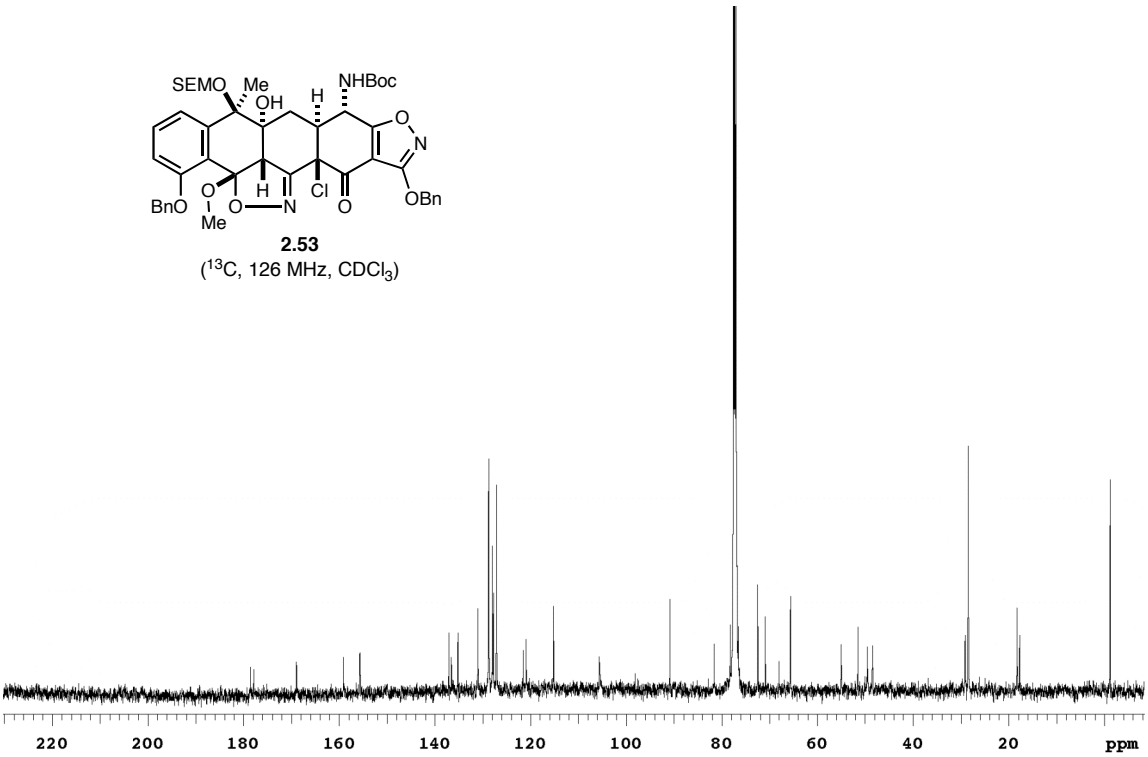

**2.51**

(HSQC, 500 MHz, THF-$D_8$)

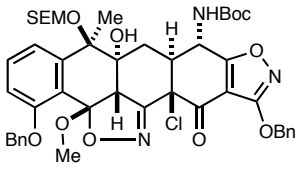




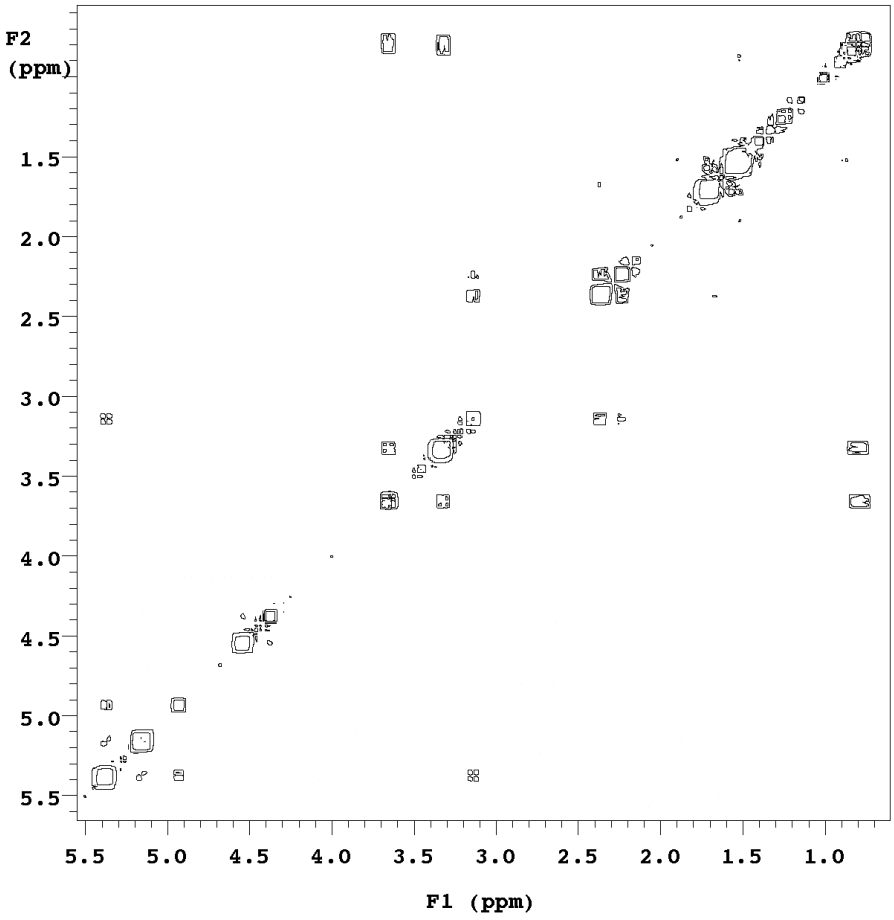

**2.53**
($^1$H, 600 MHz, $CDCl_3$)

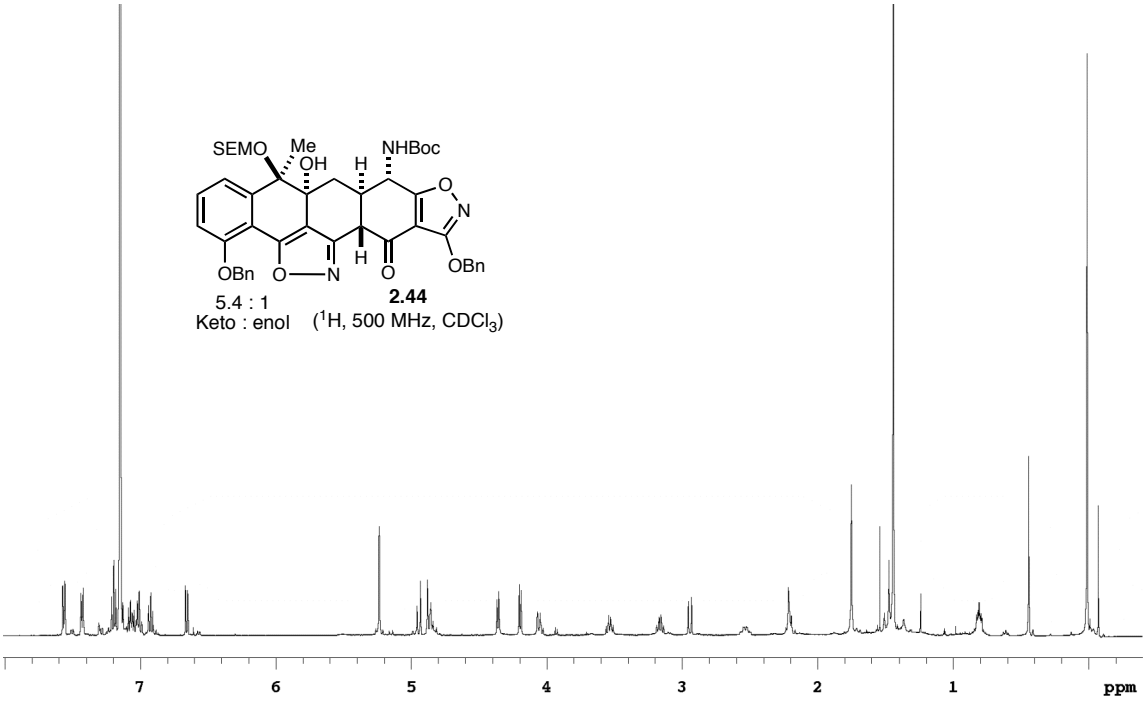



**2.53**
($^{13}$C, 126 MHz, $CDCl_3$)




**2.53**
(COSY, 600 MHz, $CDCl_3$)

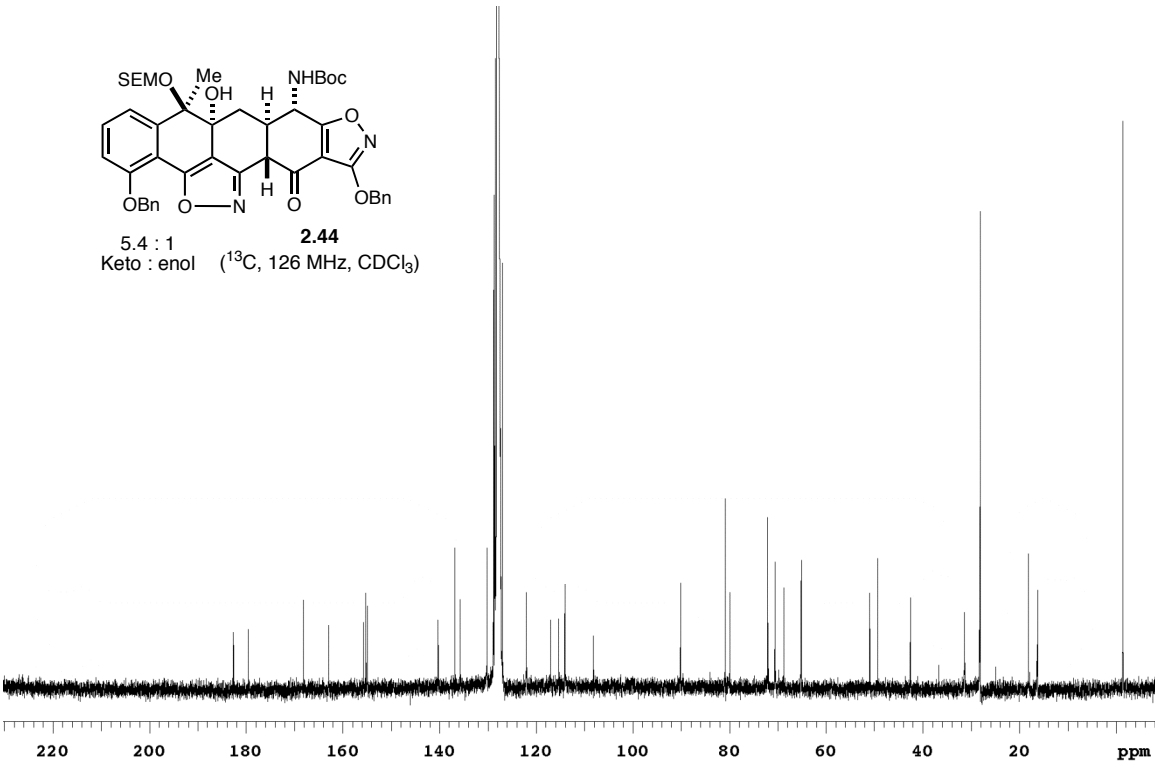





5.4 : 1
Keto : enol

**2.44**

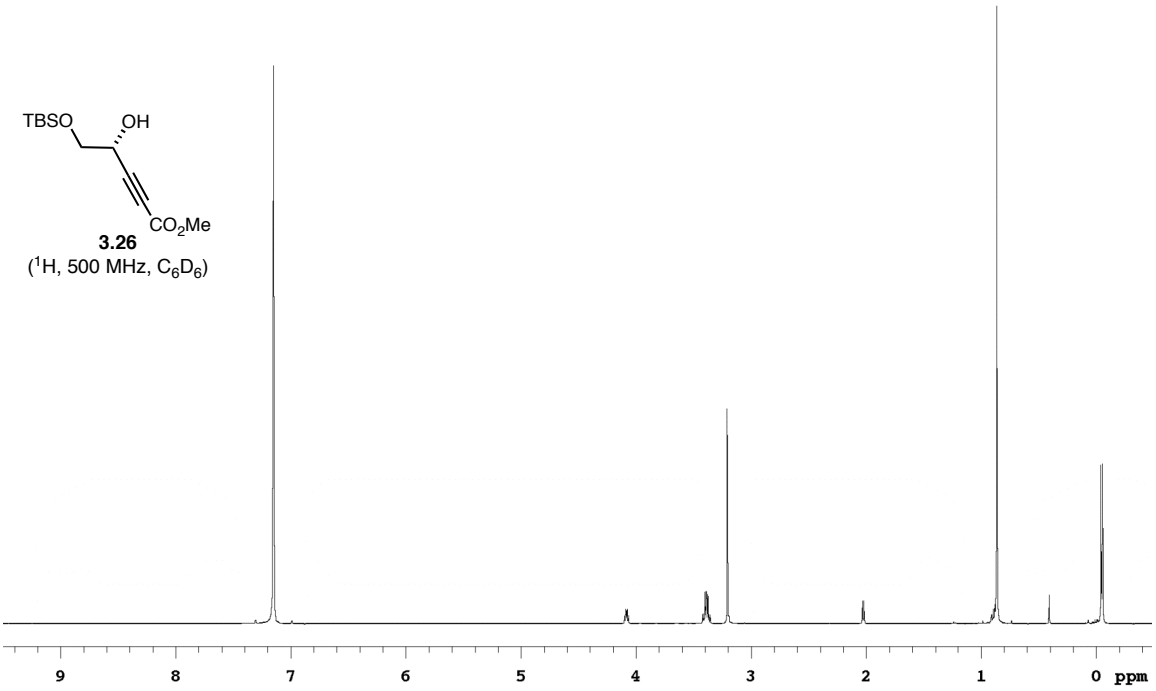
($^1$H, 500 MHz, $CDCl_3$)

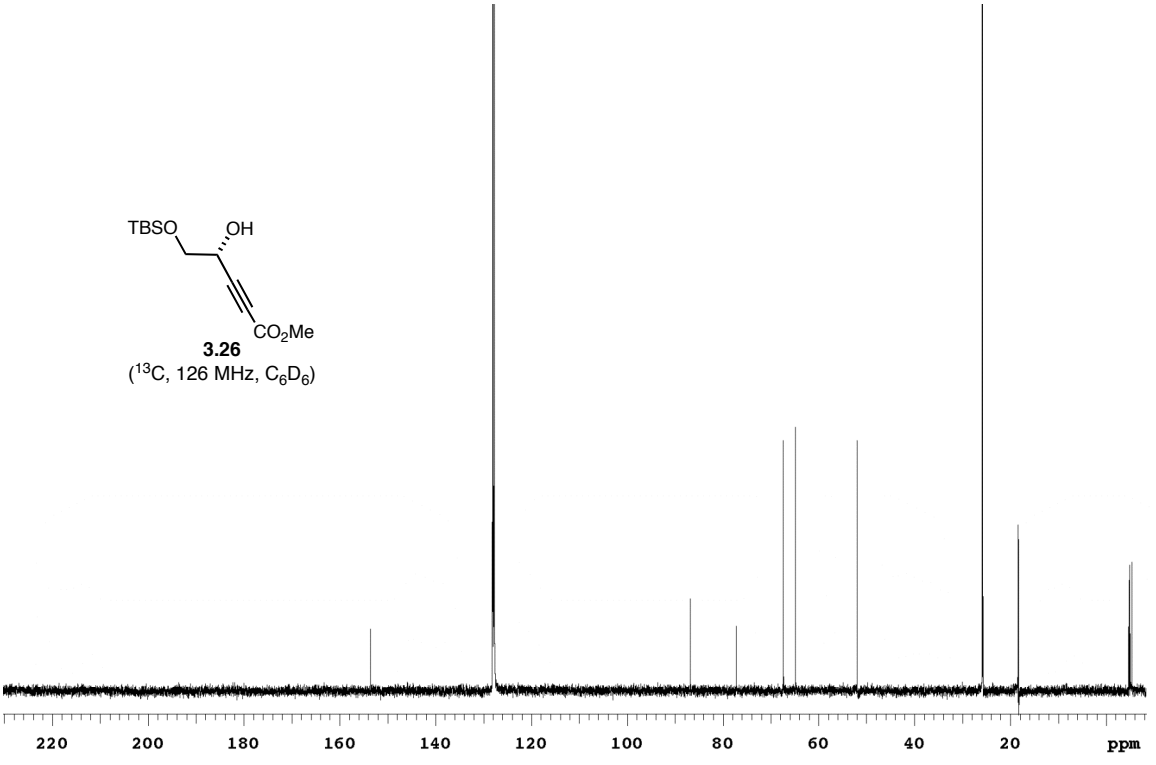


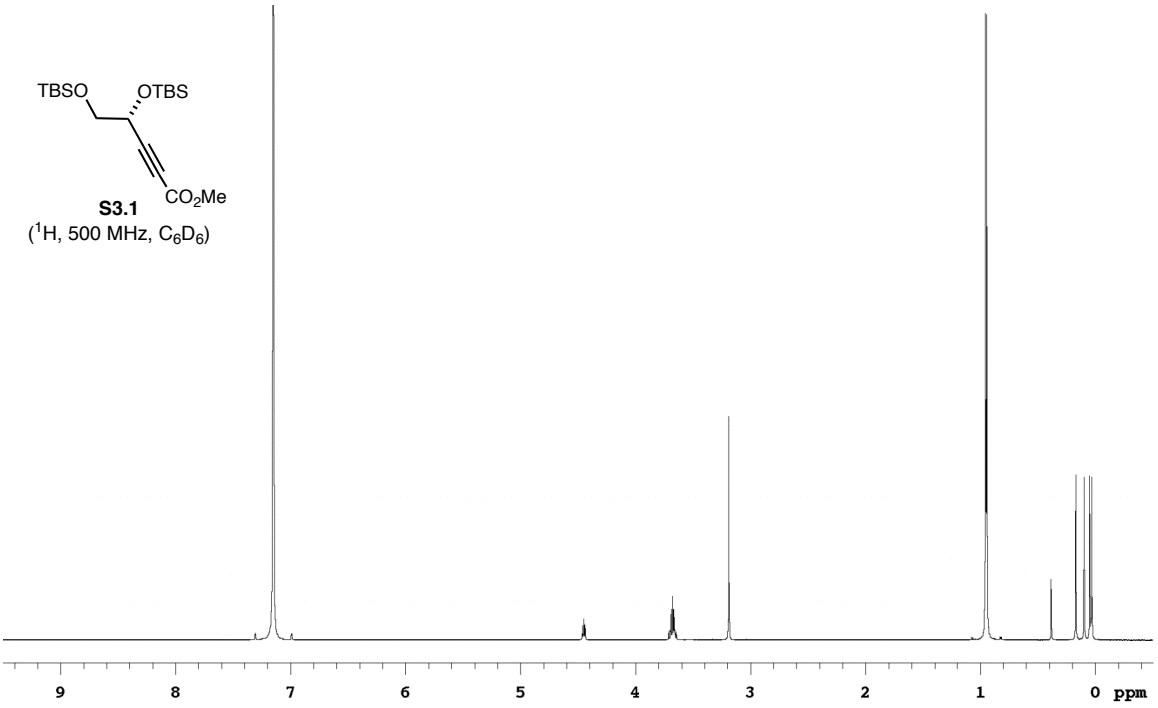

5.4 : 1
Keto : enol

**2.44**

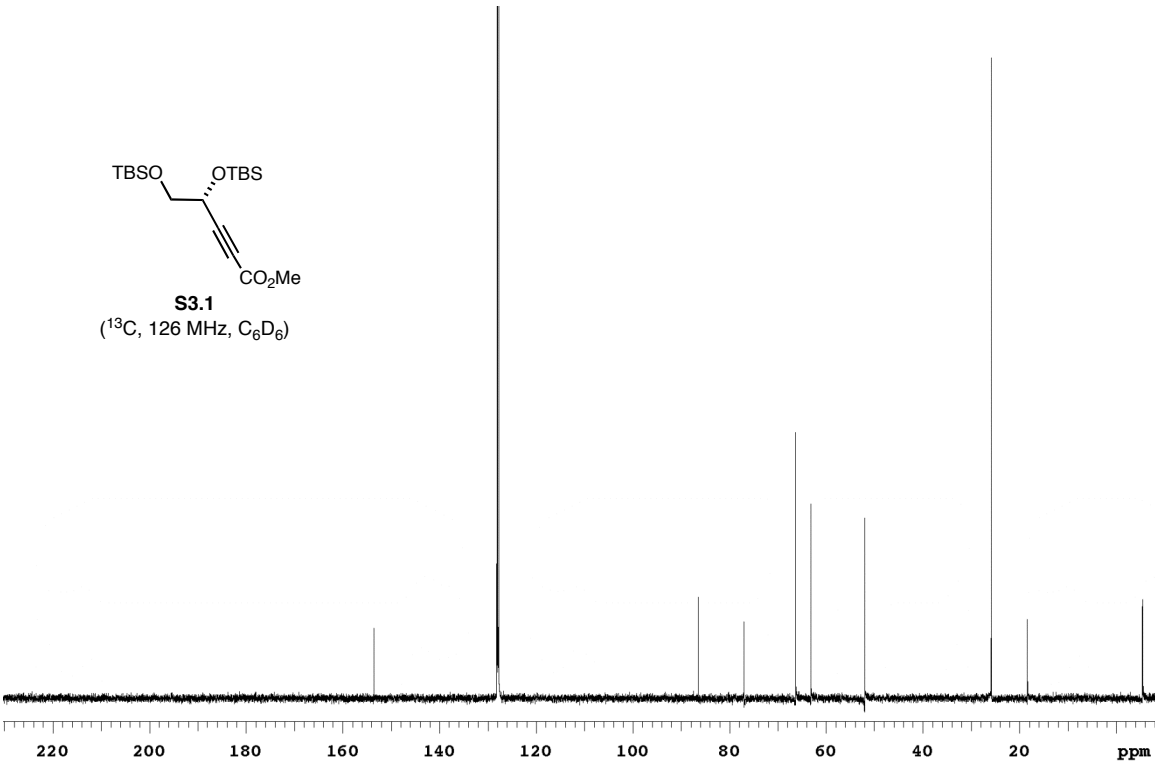
($^{13}$C, 126 MHz, $CDCl_3$)


TBSO
OH
CO2Me
3.26
(1H, 500 MHz, C6D6)
9
8
7
6
5
4
3
2
1
0
ppm

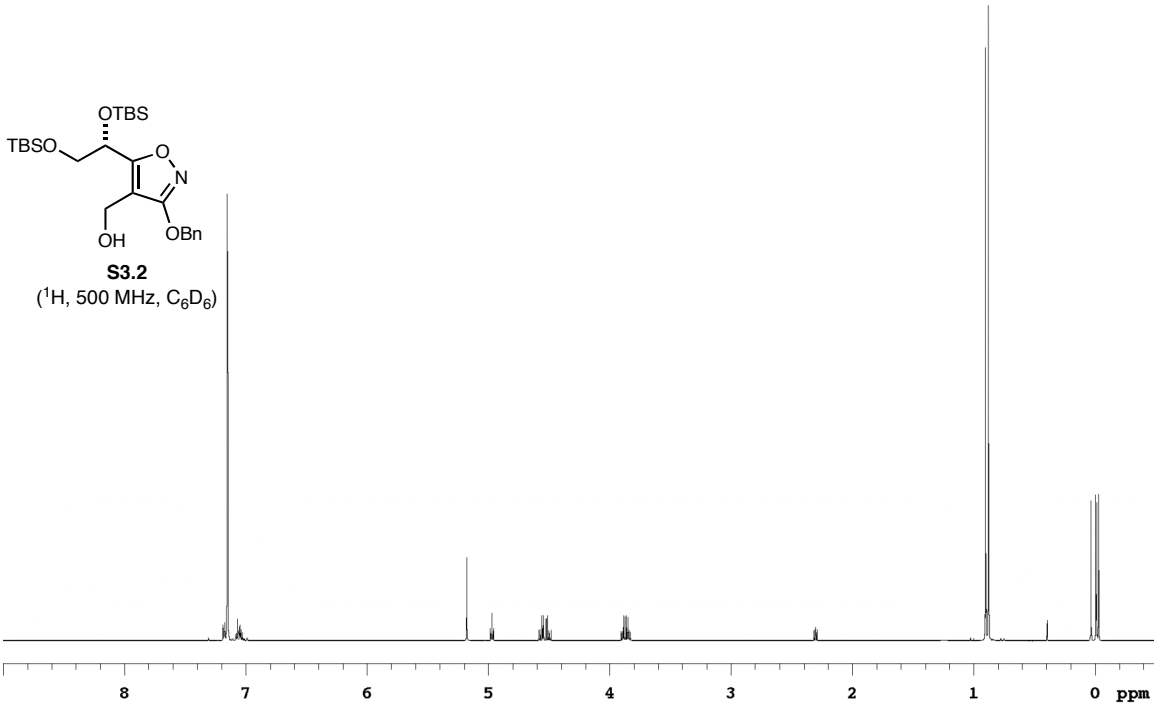

TBSO
OH
CO2Me
3.26
(13C, 126 MHz, C6D6)
220
200
180
160
140
120
100
80
60
40
20
ppm



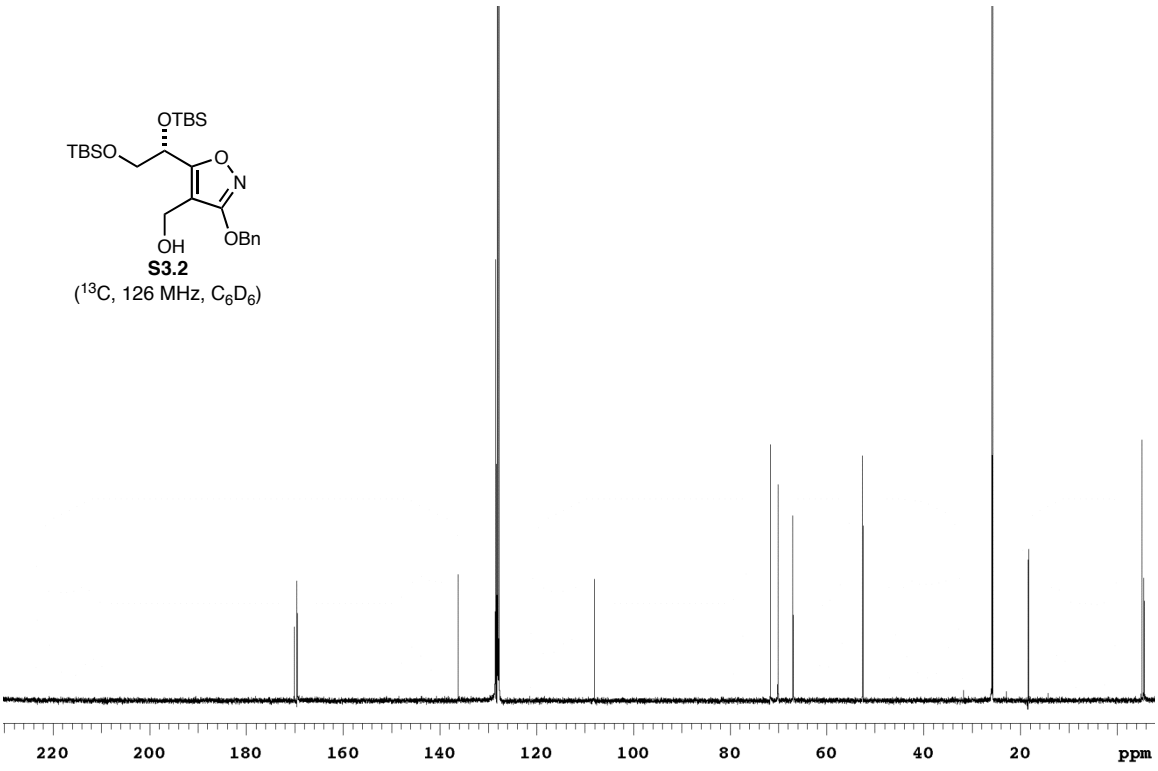

**S3.1**
($^1$H, 500 MHz, $C_6D_6$)



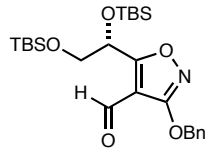

**S3.1**
($^{13}$C, 126 MHz, $C_6D_6$)




**S3.2**
($^1$H, 500 MHz, $C_6D_6$)

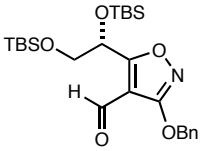



**S3.2**
($^{13}$C, 126 MHz, $C_6D_6$)

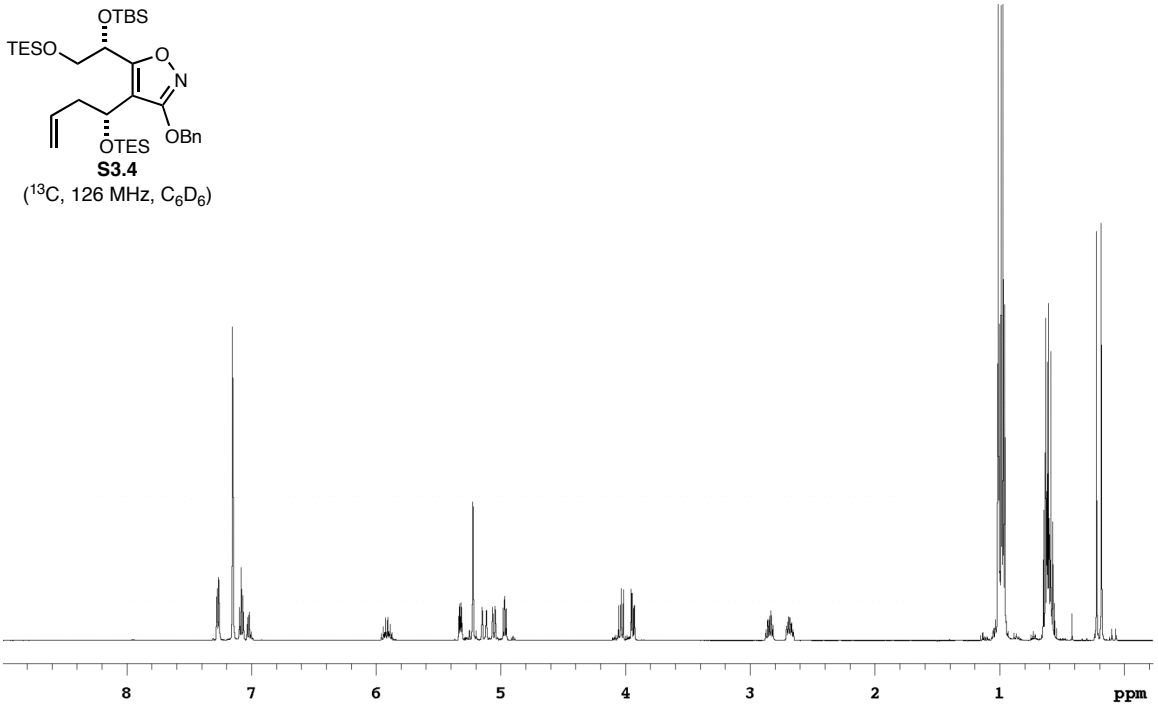


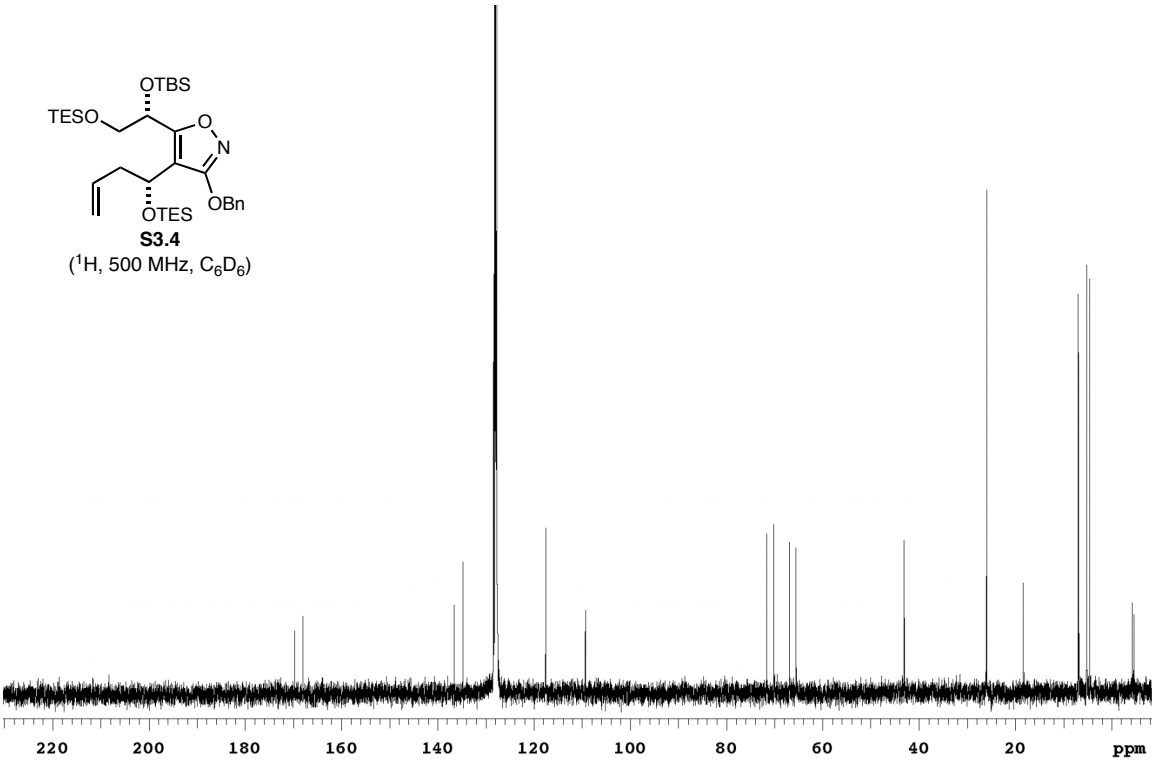

**S3.3**
($^1$H, 500 MHz, $C_6D_6$)

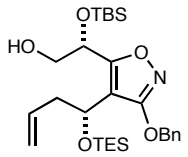



**S3.3**
($^{13}$C, 126 MHz, $C_6D_6$)


OTBS
TESO
O
N
OBn
OTES
S3.4
(13C, 126 MHz, C6D6)
8
7
6
5
4
3
2
1
ppm

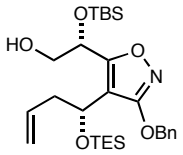

OTBS
TESO
O
N
OBn
OTES
S3.4
(1H, 500 MHz, C6D6)
220
200
180
160
140
120
100
80
60
40
20
ppm




**3.28**

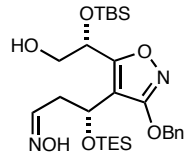
($^{1}$H, 500 MHz, $C_6D_6$)




**3.28**

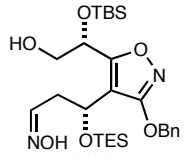
($^{13}$C, 126 MHz, $C_6D_6$)




**3.23**

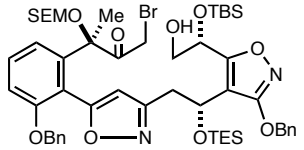
($^1$H, 600 MHz, $C_6D_6$)




**3.23**

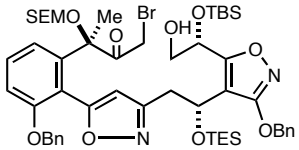
($^{13}$C, 126 MHz, $C_6D_6$)




**3.29**

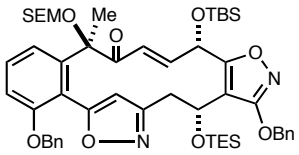
($^1$H, 500 MHz, $C_6D_6$)




**3.29**

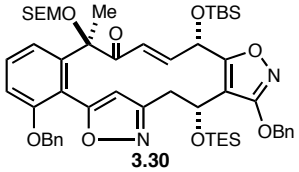
($^{13}$C, 126 MHz, $C_6D_6$)




**3.30**

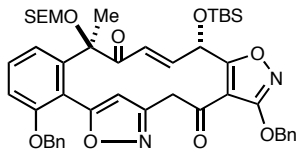
($^1$H, 500 MHz, $D_6$-DMSO)




**3.30**

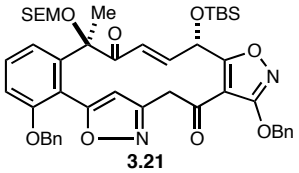
($^{13}$C, 126 MHz, $D_6$-DMSO)




**3.21**

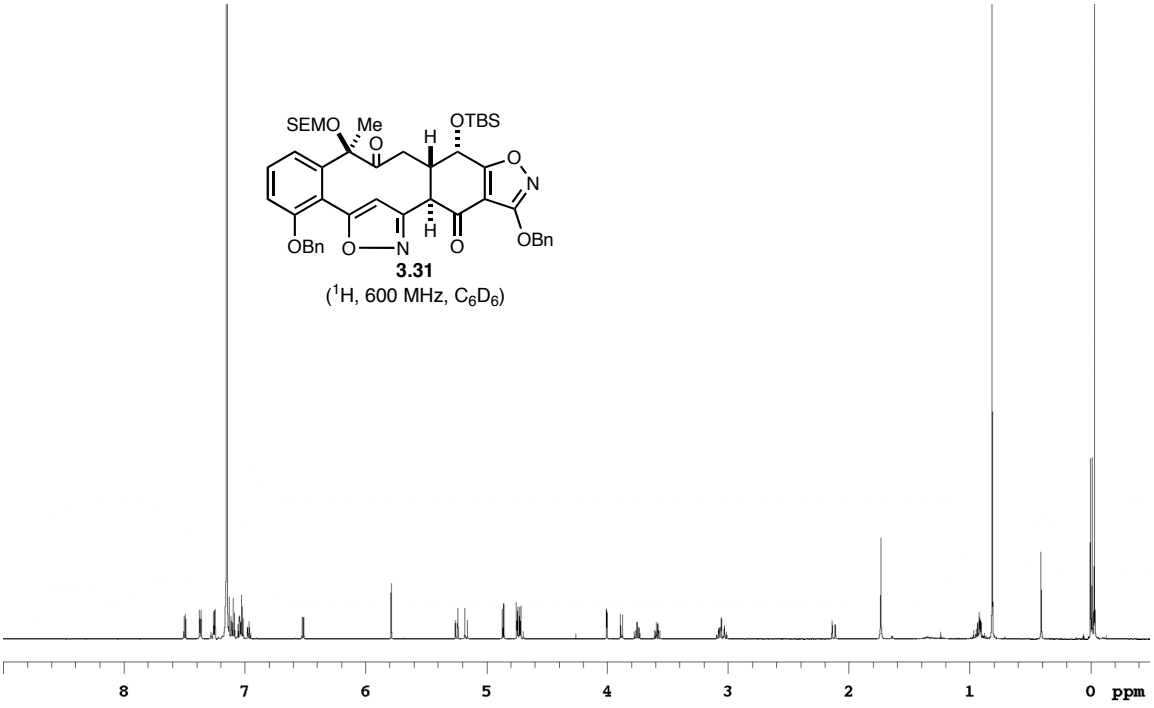
($^1$H, 500 MHz, $D_6$-DMSO)



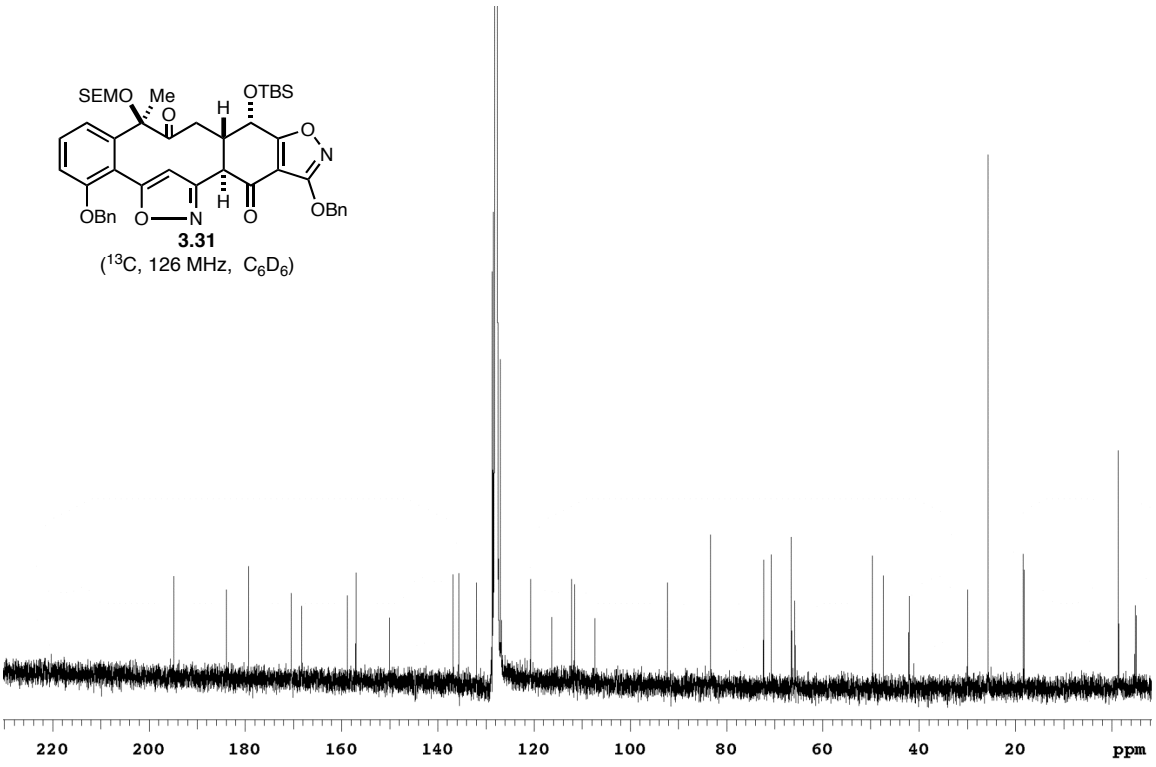

**3.21**

($^{13}$C, 126 MHz, $D_6$-DMSO)



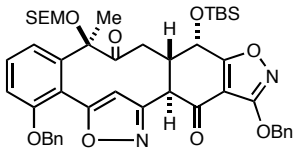

**3.31**

($^1$H, 600 MHz, $C_6D_6$)



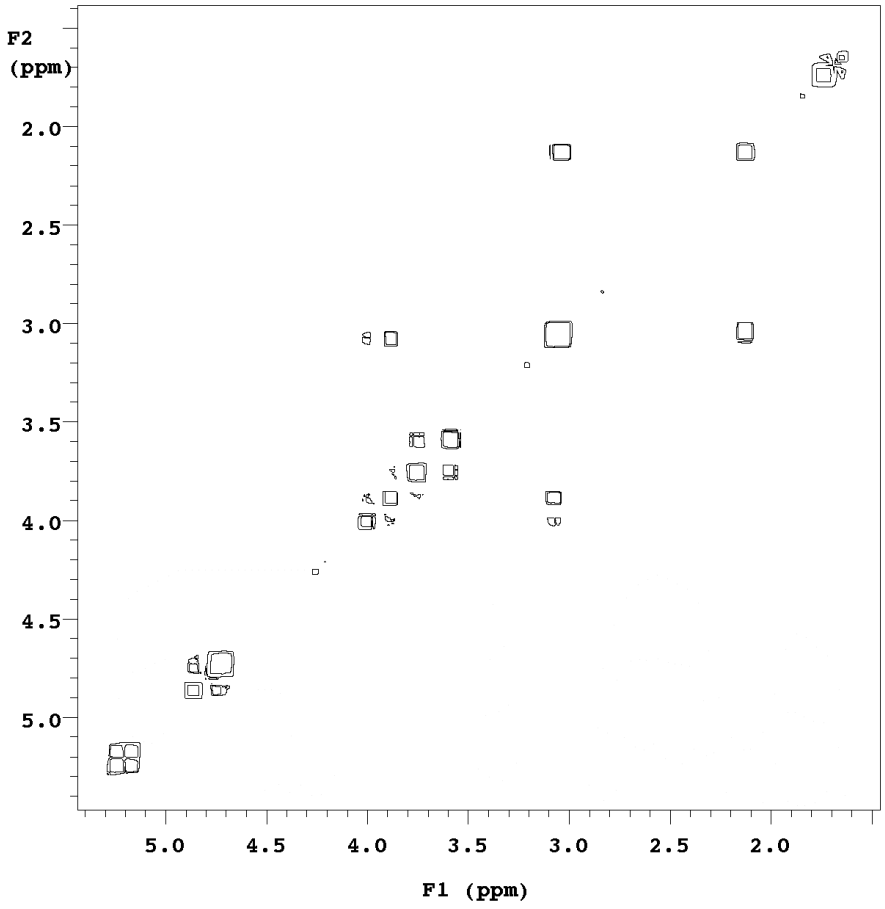

**3.31**

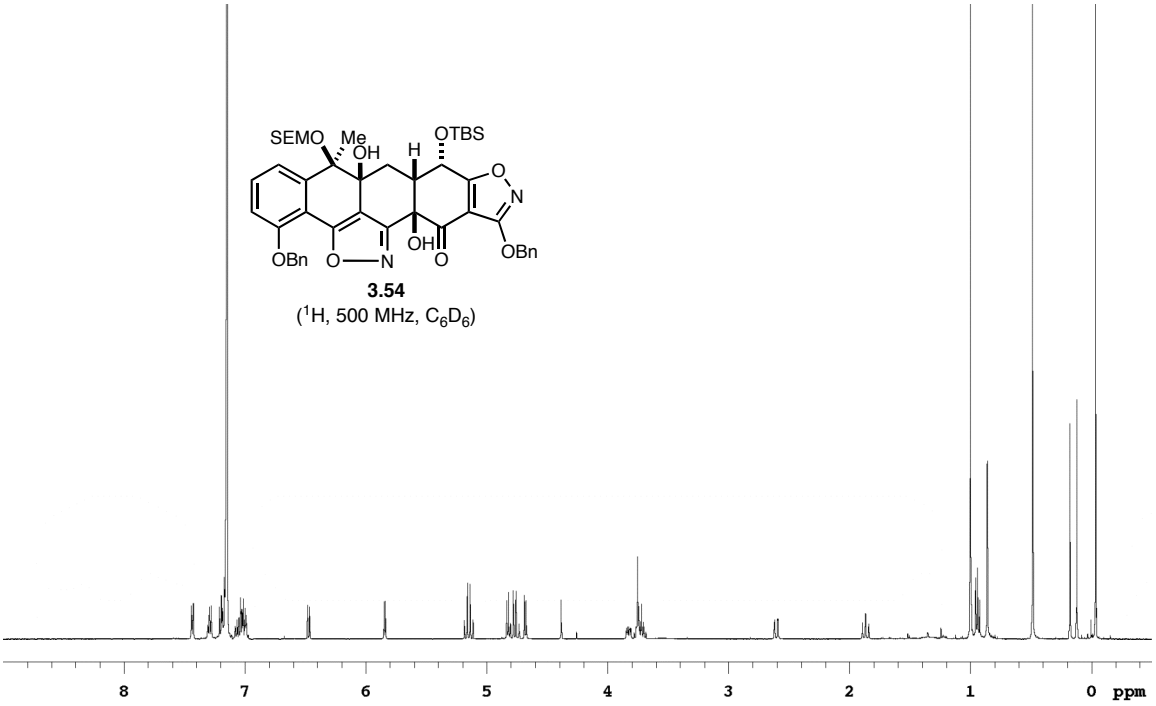
($^{13}$C, 126 MHz, $C_6D_6$)



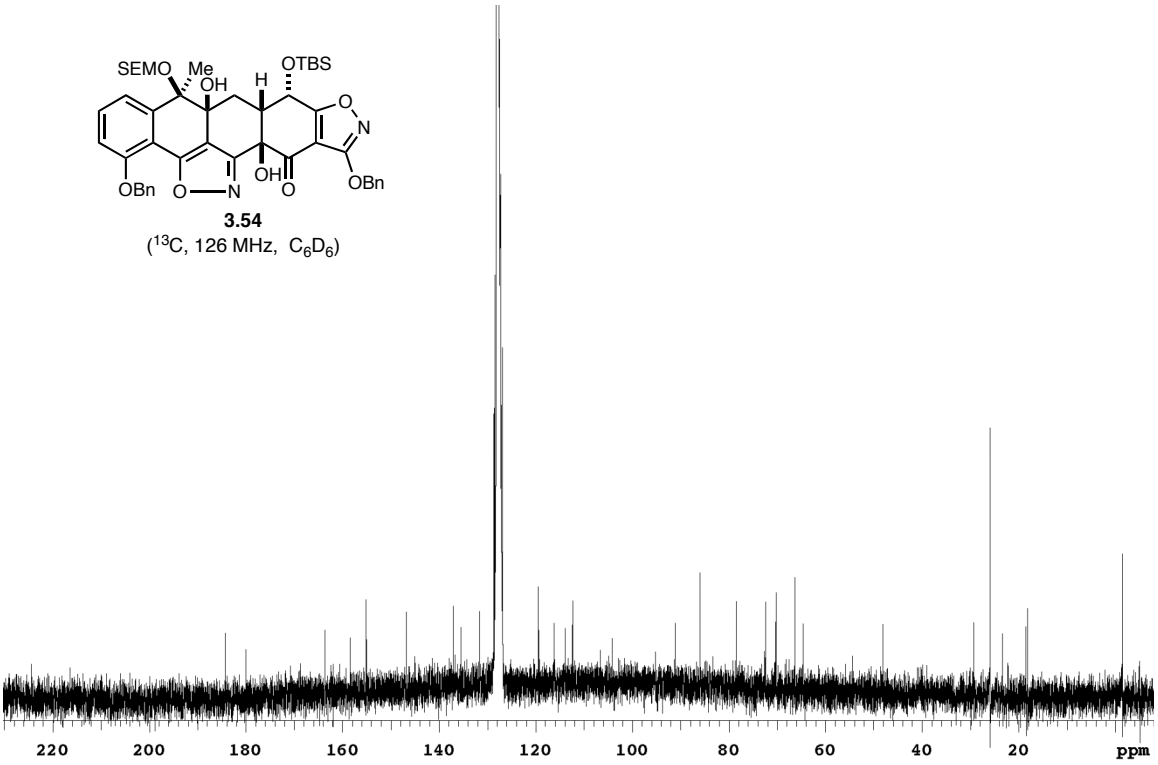

**3.31**

(COSY, 600 MHz, $C_6D_6$)

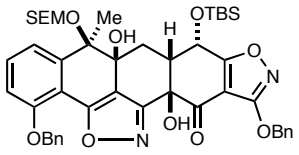




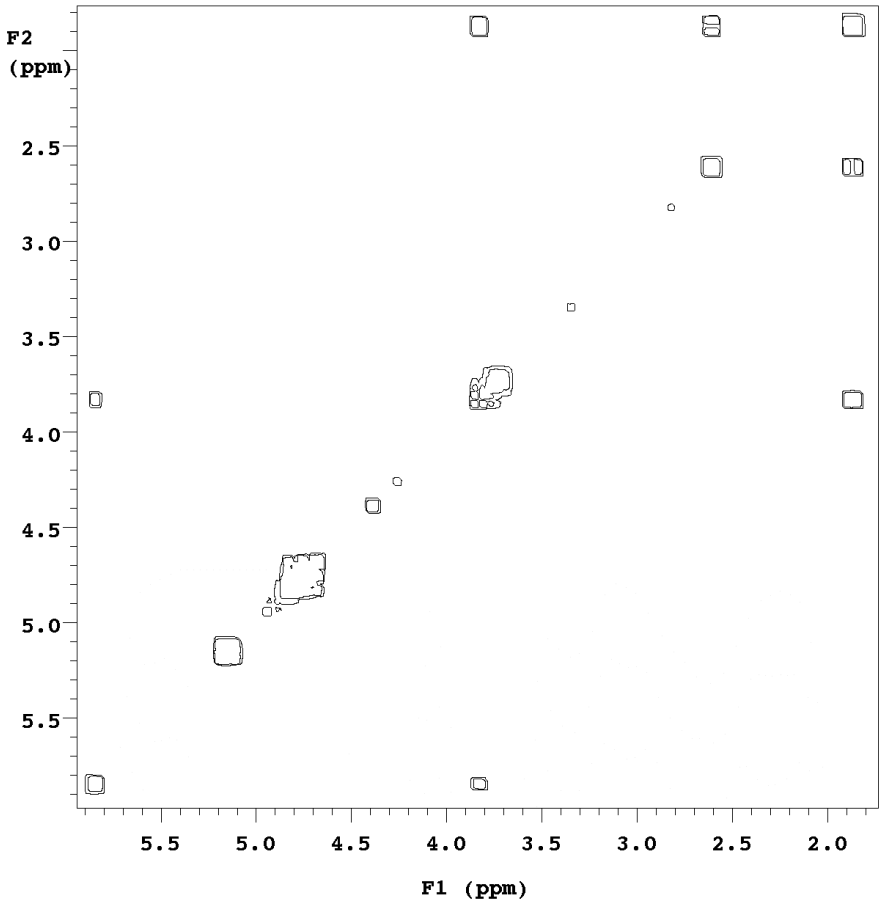

**3.54**
($^1$H, 500 MHz, $C_6D_6$)

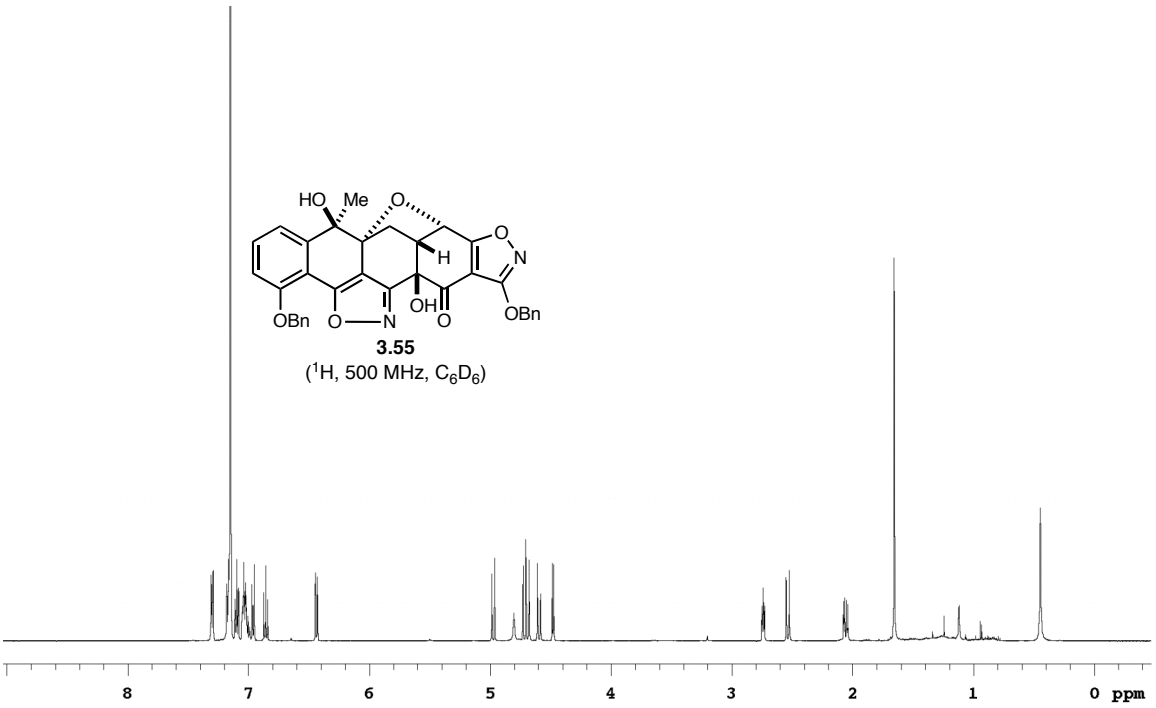



**3.54**
($^{13}$C, 126 MHz, $C_6D_6$)



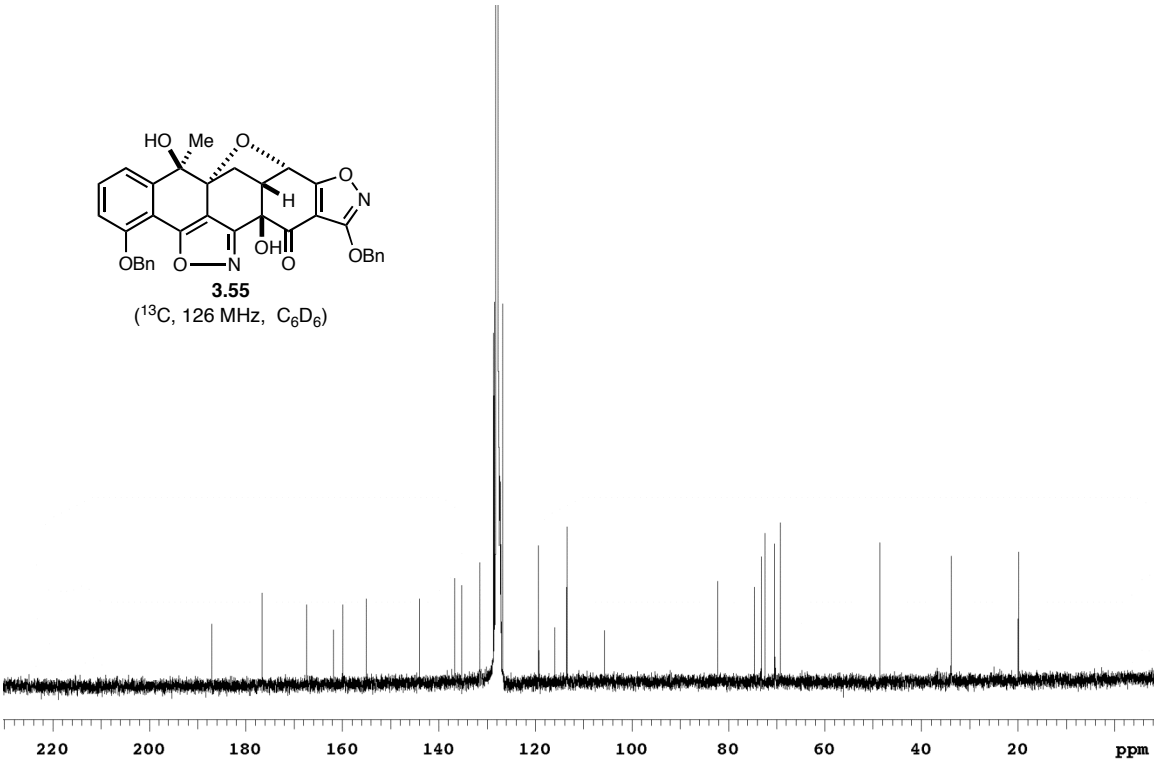

**3.54**
(COSY, 500 MHz, $C_6D_6$)





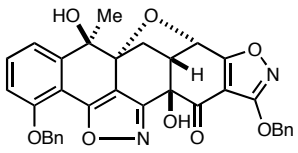

**3.55**

($^{1}$H, 500 MHz, $C_6D_6$)



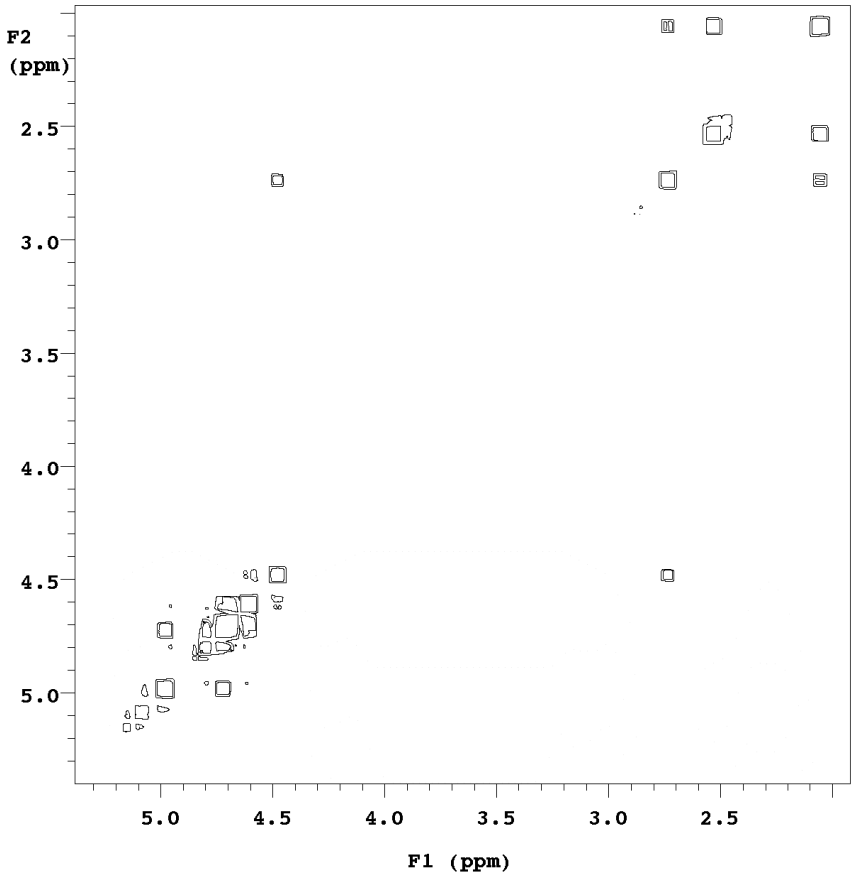

**3.55**

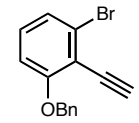
($^{13}$C, 126 MHz, $C_6D_6$)




**3.55**

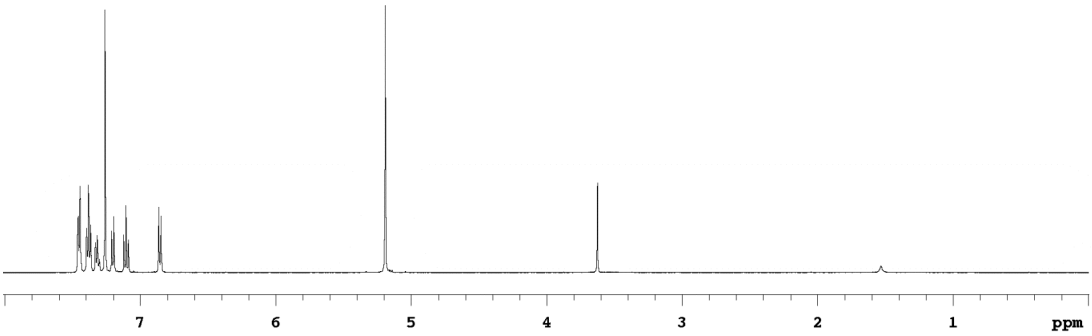
(COSY, 600 MHz, $C_6D_6$)

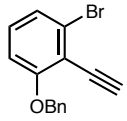





**3.67**

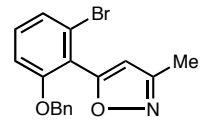
($^1$H, 500 MHz, $CDCl_3$)




**3.67**

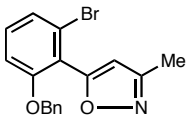
($^{13}$C, 500 MHz, $CDCl_3$)




**S3.5**

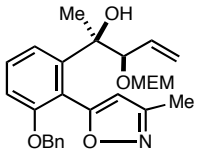
($^1$H, 500 MHz, $CDCl_3$)



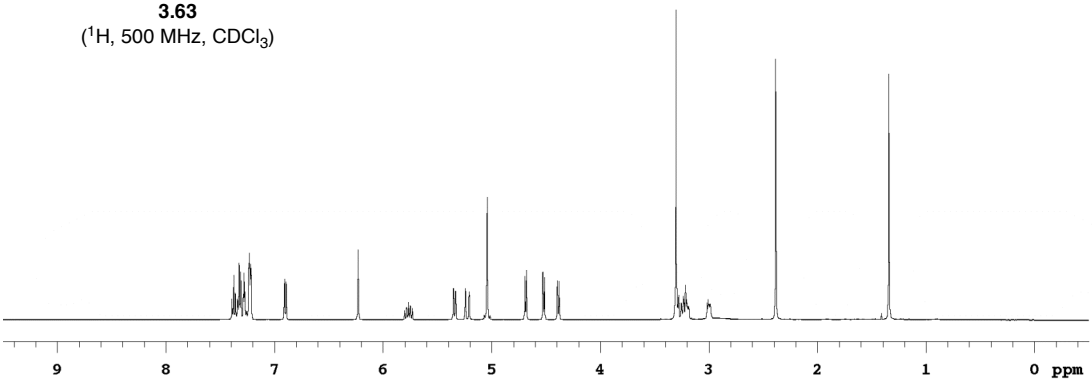

**S3.5**

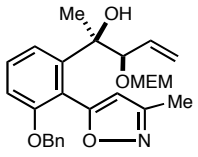
($^{13}$C, 126 MHz, $CDCl_3$)




**3.63**

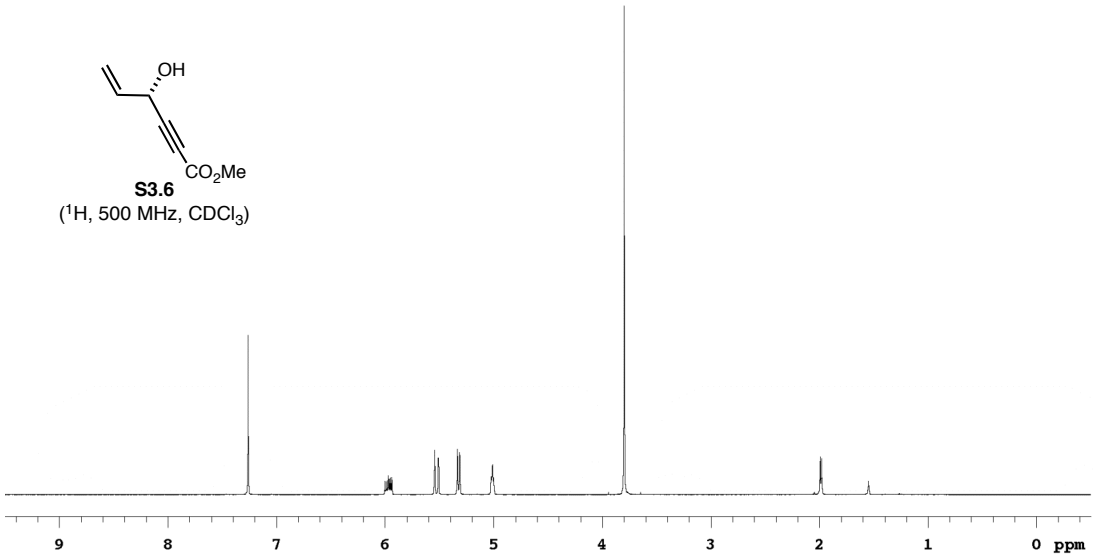
($^1$H, 500 MHz, $CDCl_3$)



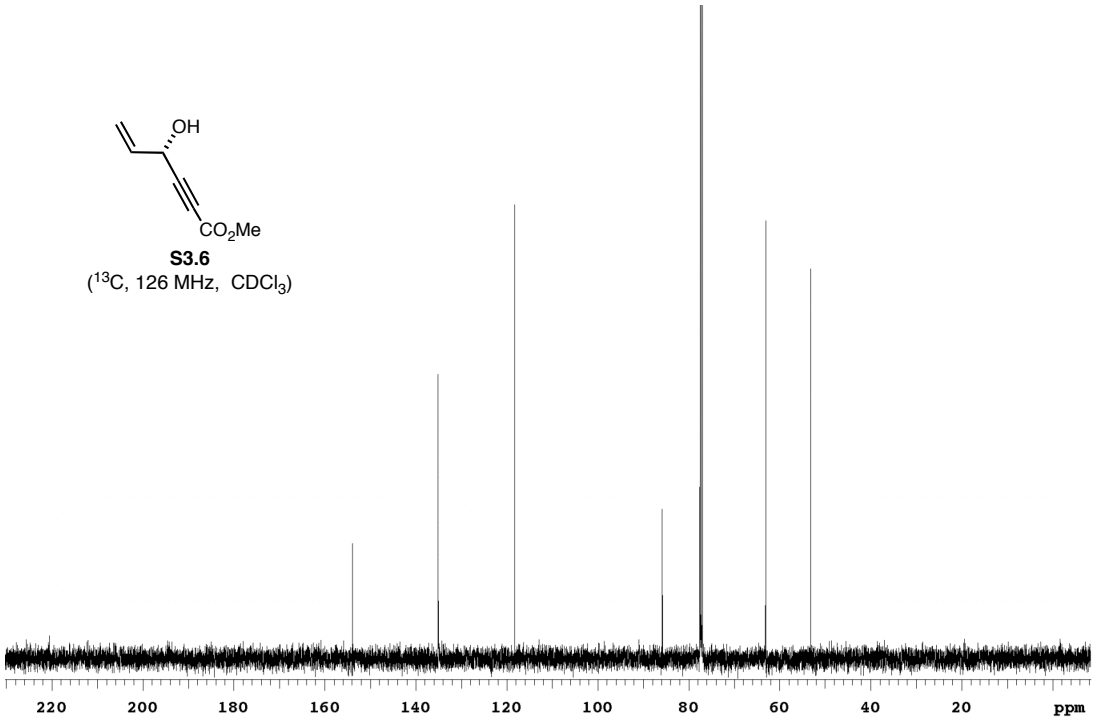




**3.63**

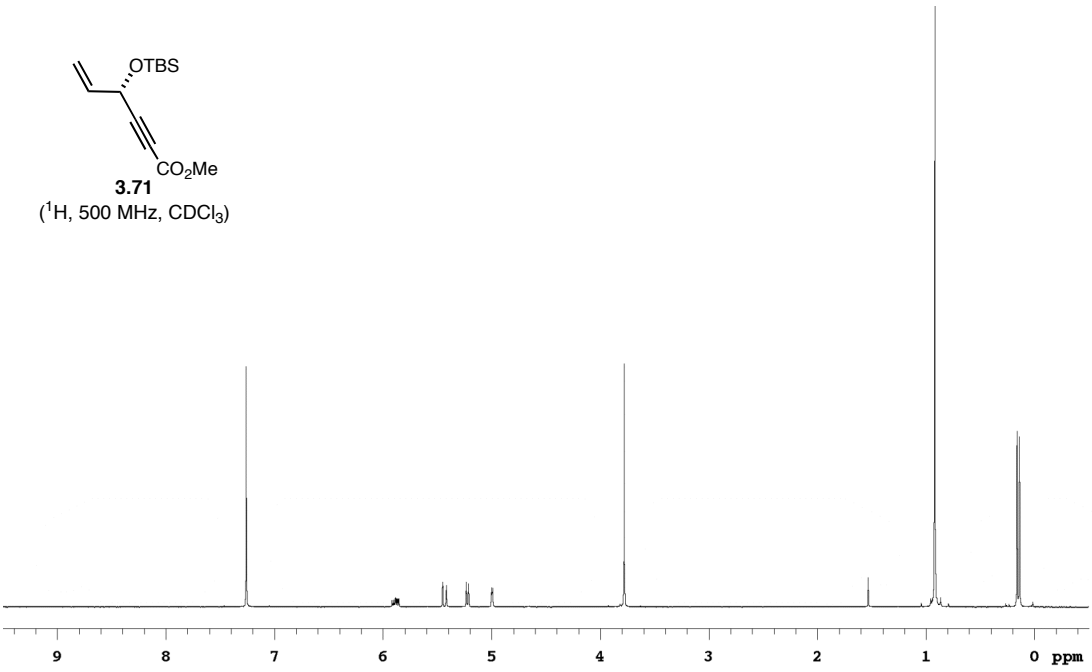
($^{13}$C, 126 MHz, $CDCl_3$)



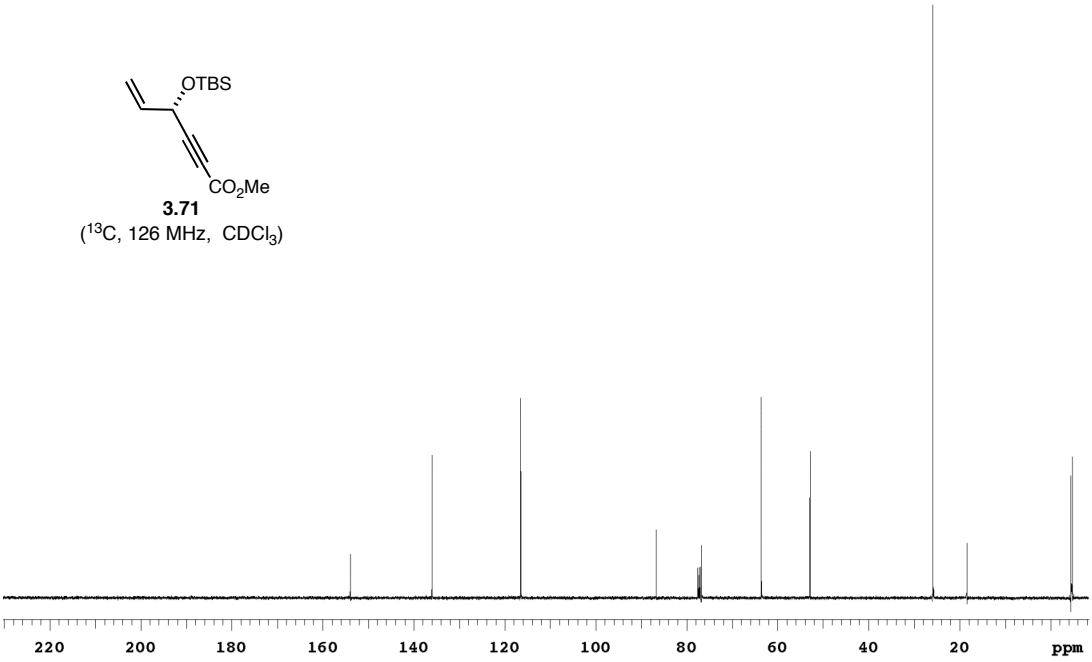

**S3.6**
($^1$H, 500 MHz, $CDCl_3$)



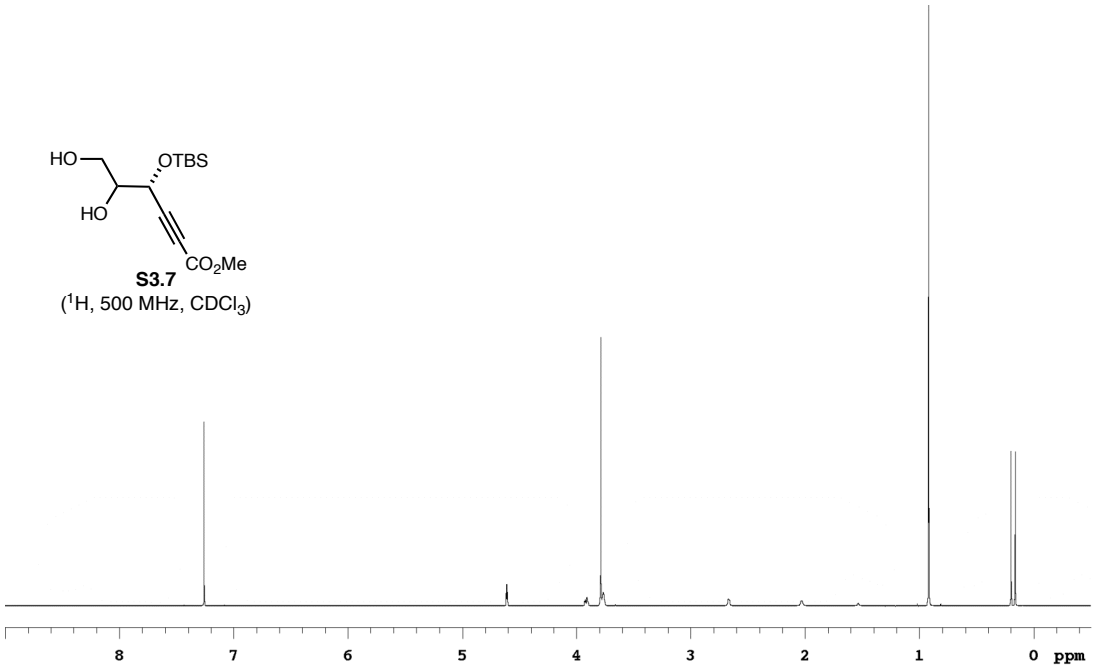

**S3.6**
($^{13}$C, 126 MHz, $CDCl_3$)



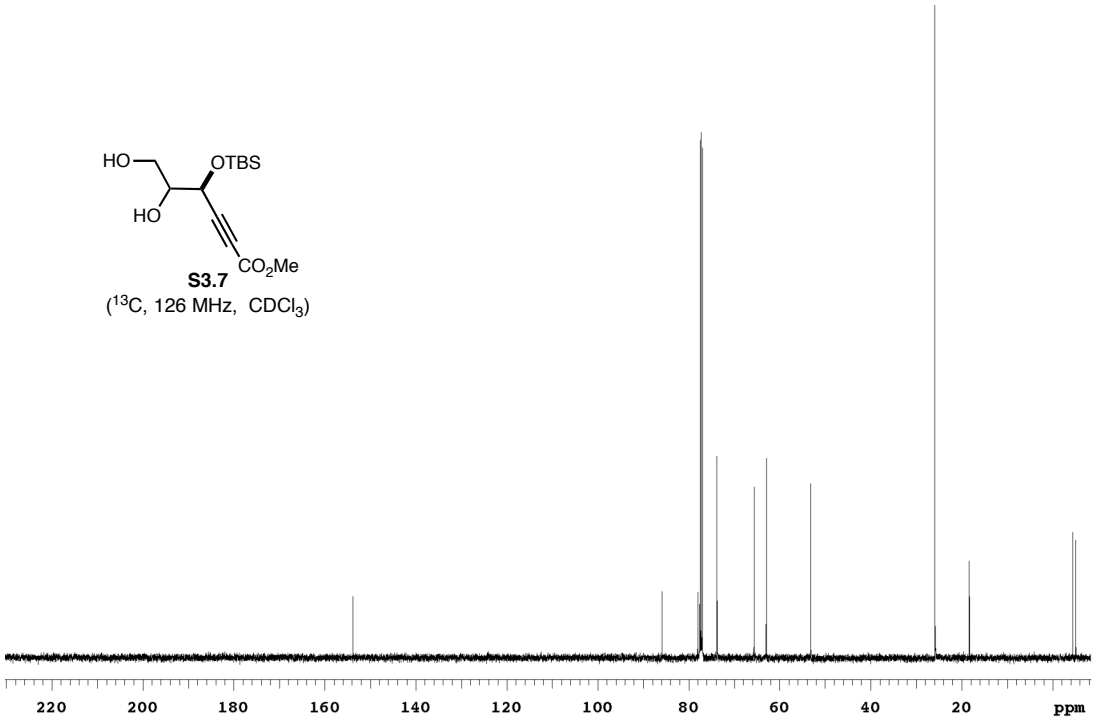

**3.71**
($^1$H, 500 MHz, $CDCl_3$)



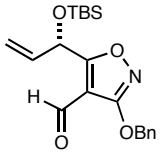

**3.71**
($^{13}$C, 126 MHz, $CDCl_3$)




**S3.7**
($^1$H, 500 MHz, $CDCl_3$)

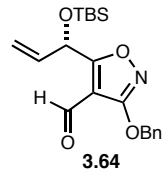



**S3.7**
($^{13}$C, 126 MHz, $CDCl_3$)

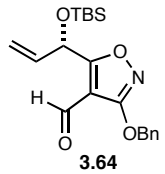



**3.64**
($^1$H, 500 MHz, $C_6D_6$)



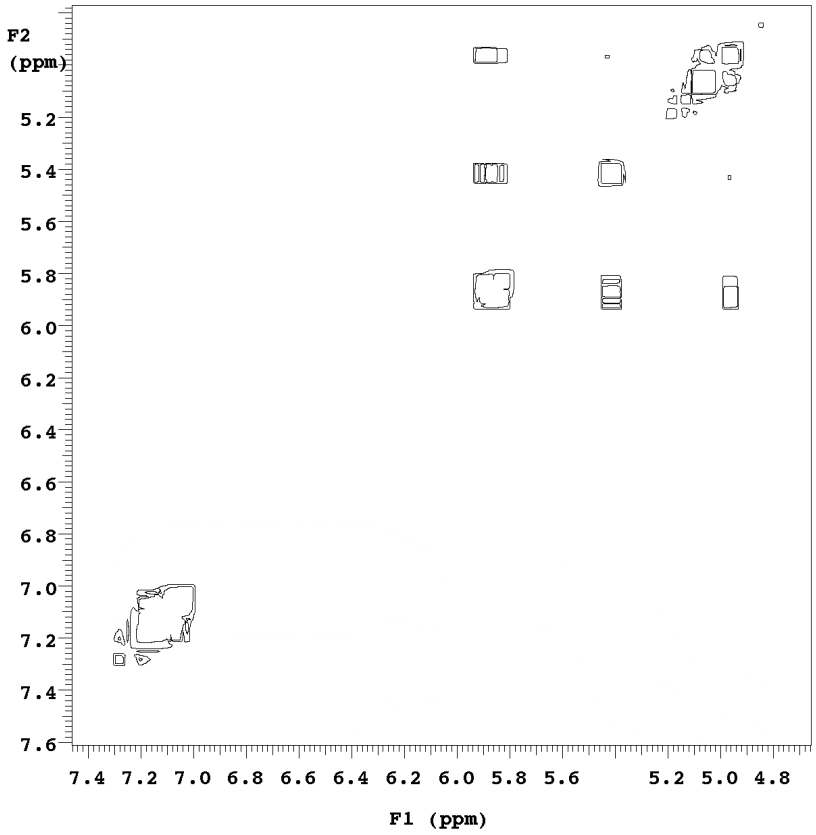



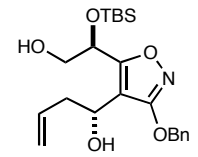

**3.64**
($^{13}$C, 126 MHz, $C_6D_6$)




**3.64**

(COSY, 600 MHz, $C_6D_6$)

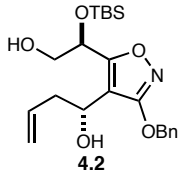





**4.2**

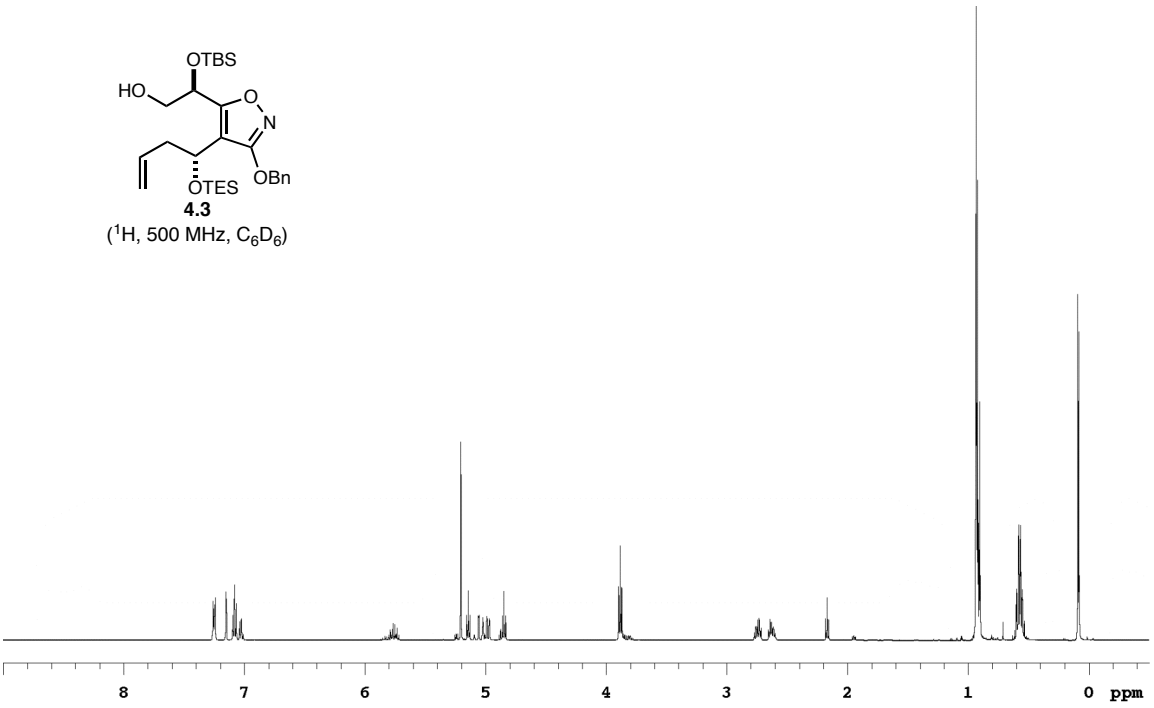
($^1$H, 500 MHz, $C_6D_6$)

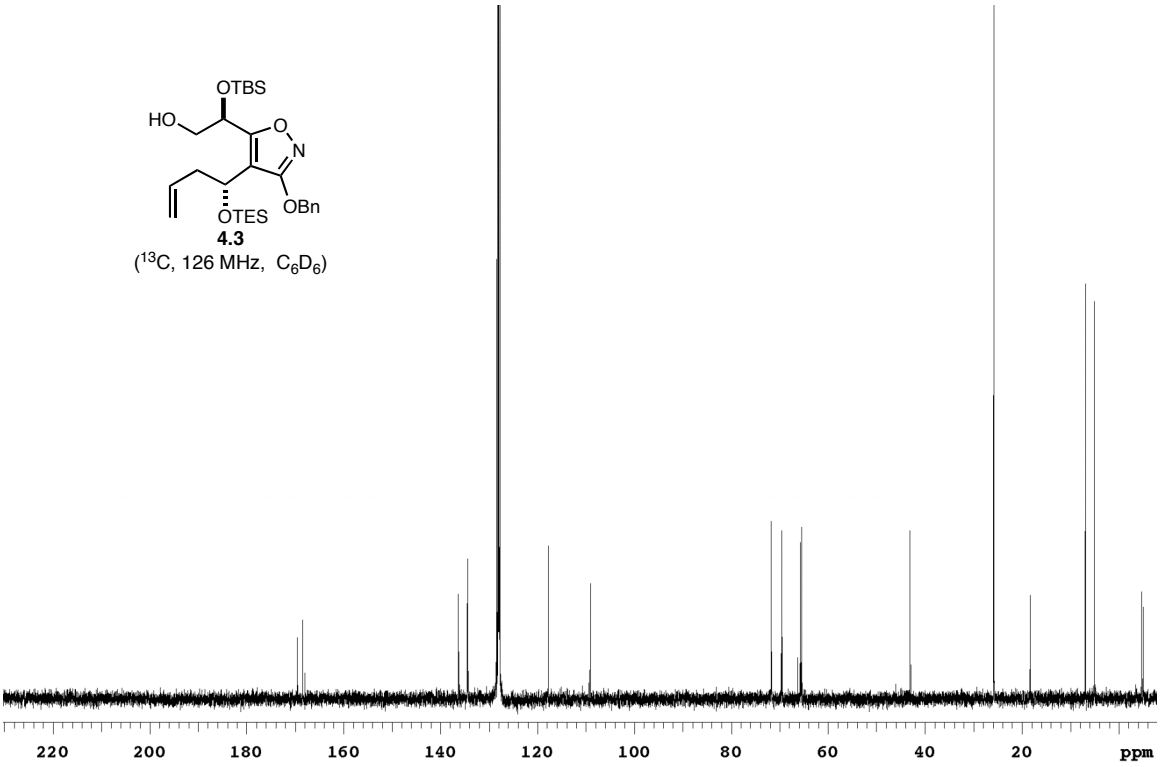


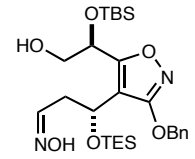




**4.2**

($^{13}$C, 126 MHz, $C_6D_6$)


OTBS
HO
O
N
OBn
OTES
4.3
(1H, 500 MHz, C6D6)
8
7
6
5
4
3
2
1
0
ppm

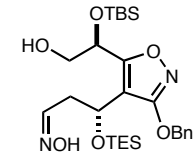

OTBS
HO
O
N
OBn
OTES
4.3
(13C, 126 MHz, C6D6)
220
200
180
160
140
120
100
80
60
40
20
ppm




**4.4**

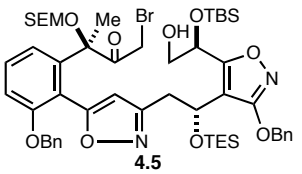
($^1$H, 500 MHz, $C_6D_6$)




**4.4**

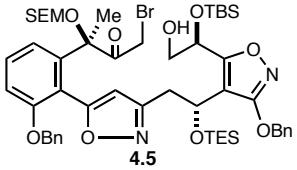
($^{13}$C, 126 MHz, $C_6D_6$)




**4.5**

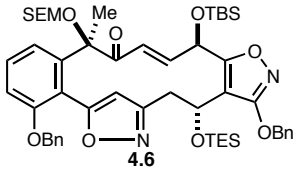
($^1$H, 600 MHz, $C_6D_6$)




**4.5**

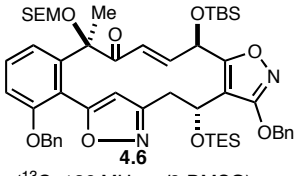
($^{13}$C, 126 MHz, $C_6D_6$)




**4.6**

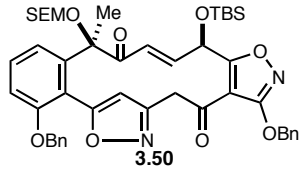
($^1$H, 500 MHz, *d*6-DMSO)




**4.6**

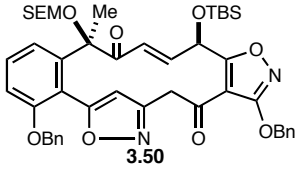
($^{13}$C, 126 MHz, *d*6-DMSO)




**3.50**

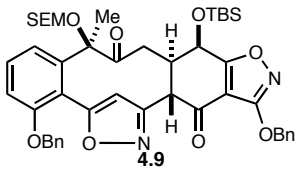
($^{1}$H, 500 MHz, D6-DMSO)




**3.50**

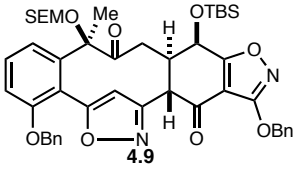
($^{13}$C, 126 MHz, D6-DMSO)




**4.9**

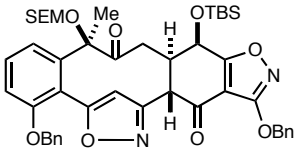
($^1$H, 600 MHz, D6-acetone)



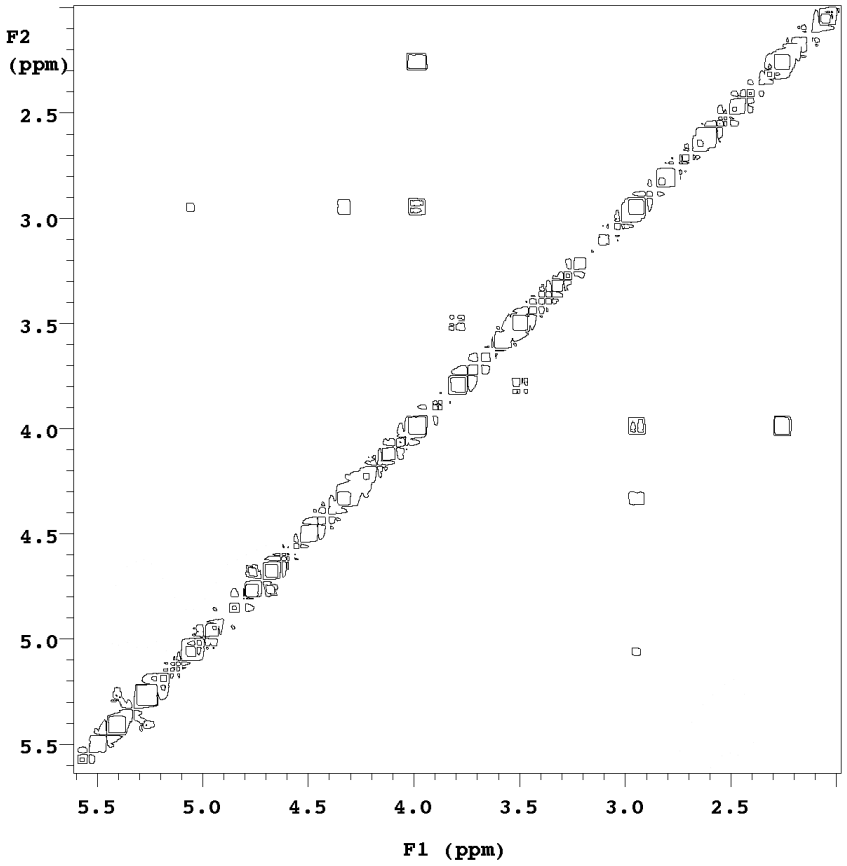

**4.9**

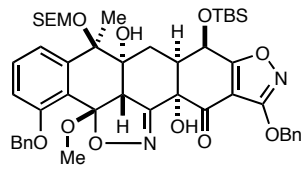
($^{13}$C, 126 MHz, D6-acetone)



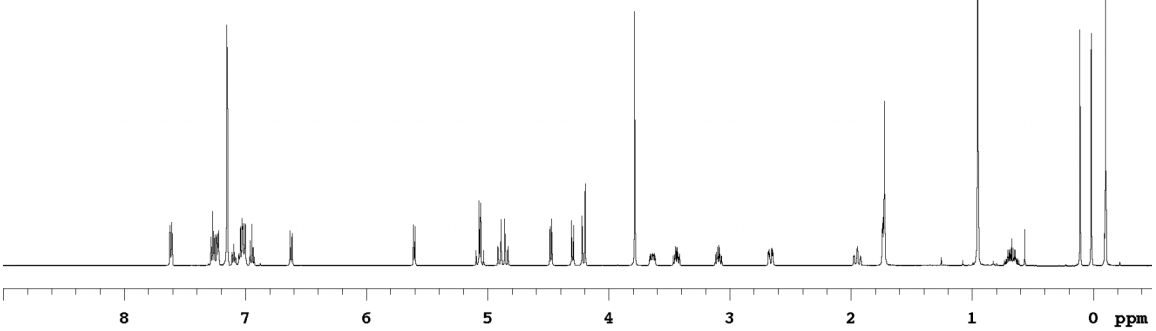

**4.9**

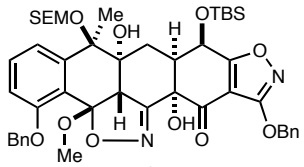
(COSY, 600 MHz, D6-acetone)



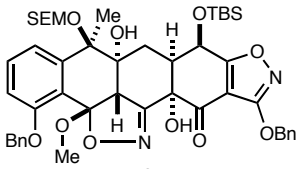



**4.10**
($^1$H, 500 MHz, $C_6D_6$)

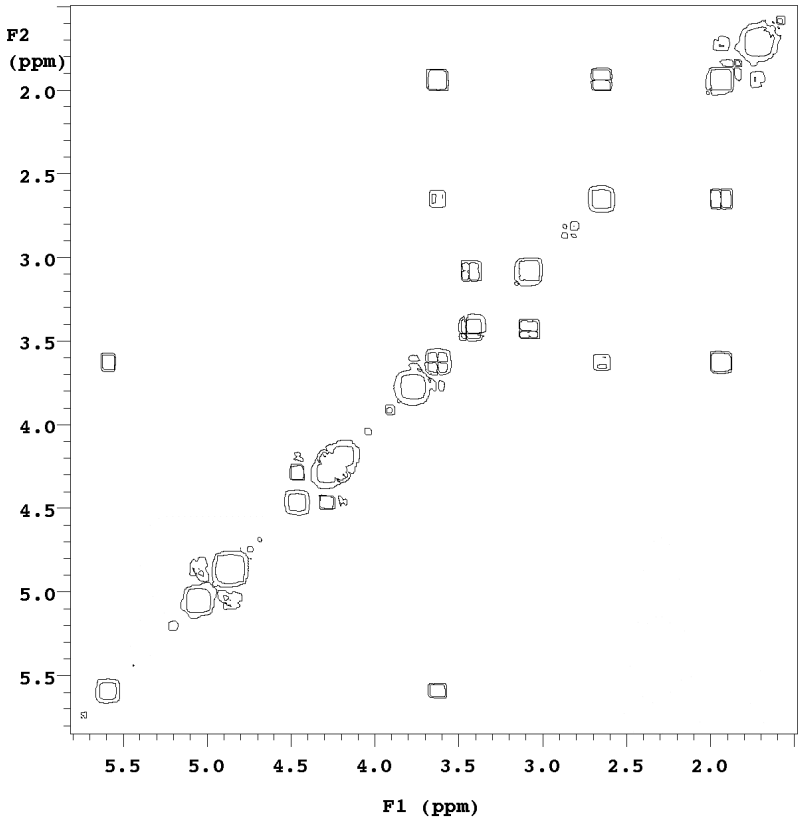


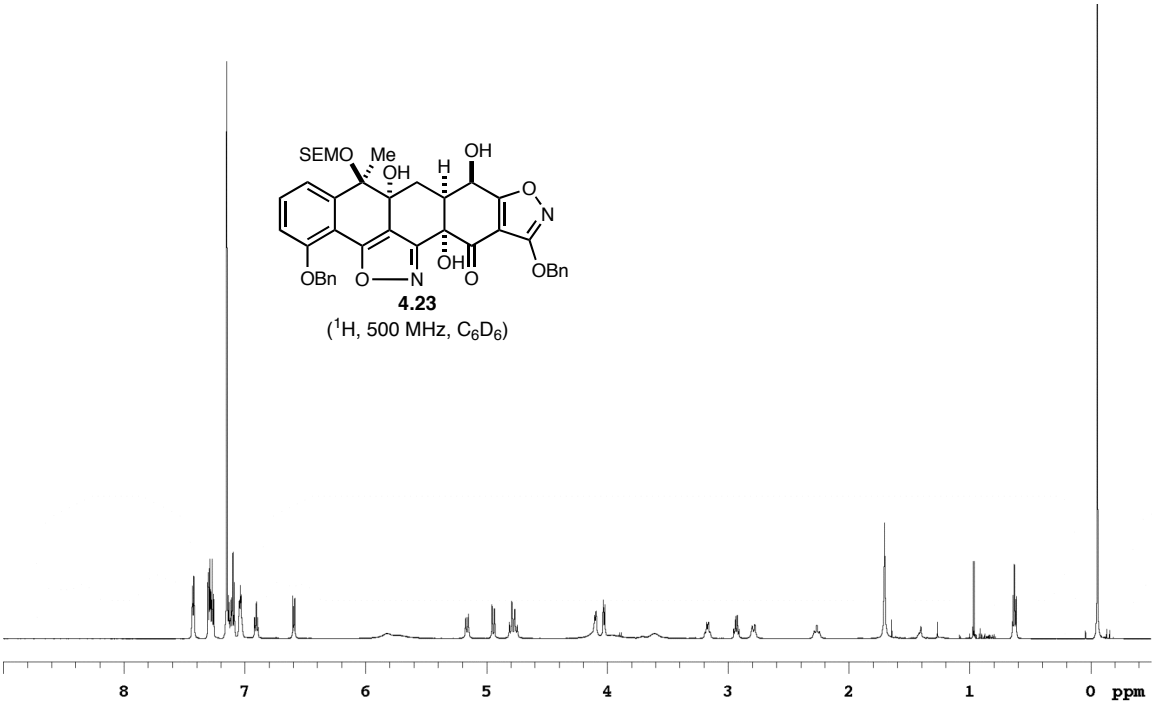




**4.10**
($^{13}$C, 126 MHz, $C_6D_6$)



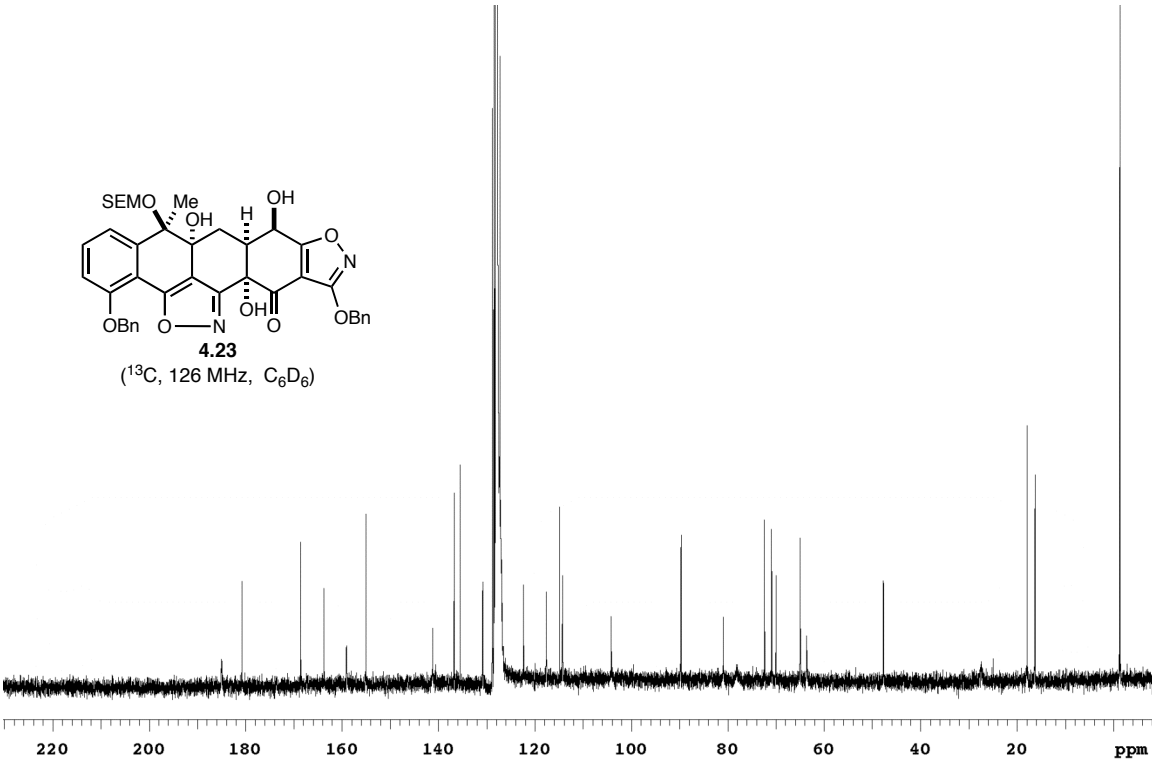

**4.10**
(COSY, 500 MHz, $C_6D_6$)





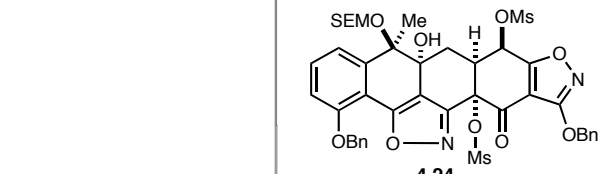

**4.23**

($^1$H, 500 MHz, $C_6D_6$)



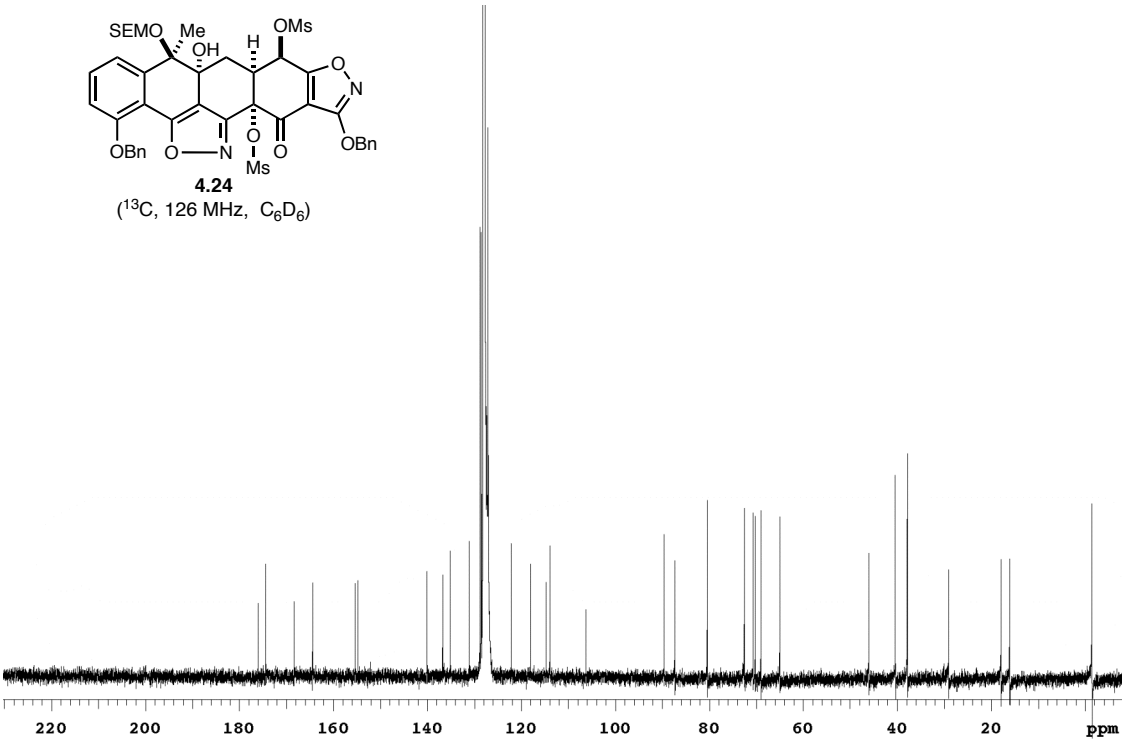

**4.23**

($^{13}$C, 126 MHz, $C_6D_6$)




**4.24**

($^1$H, 500 MHz, $C_6D_6$)

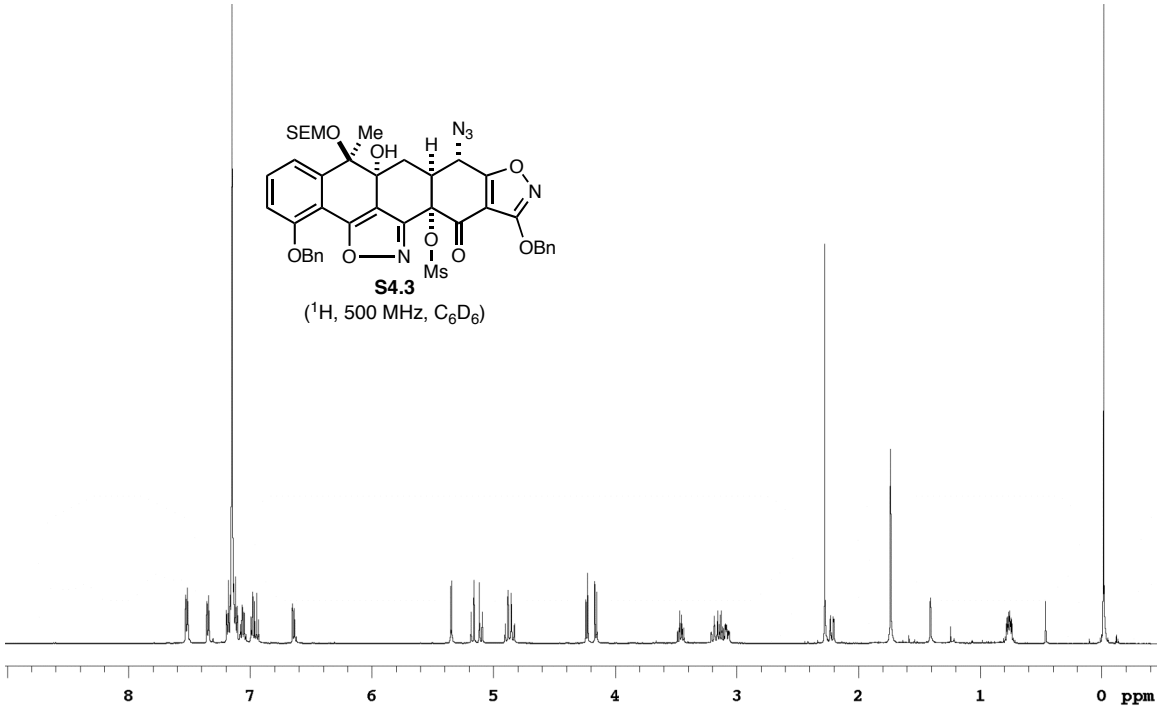






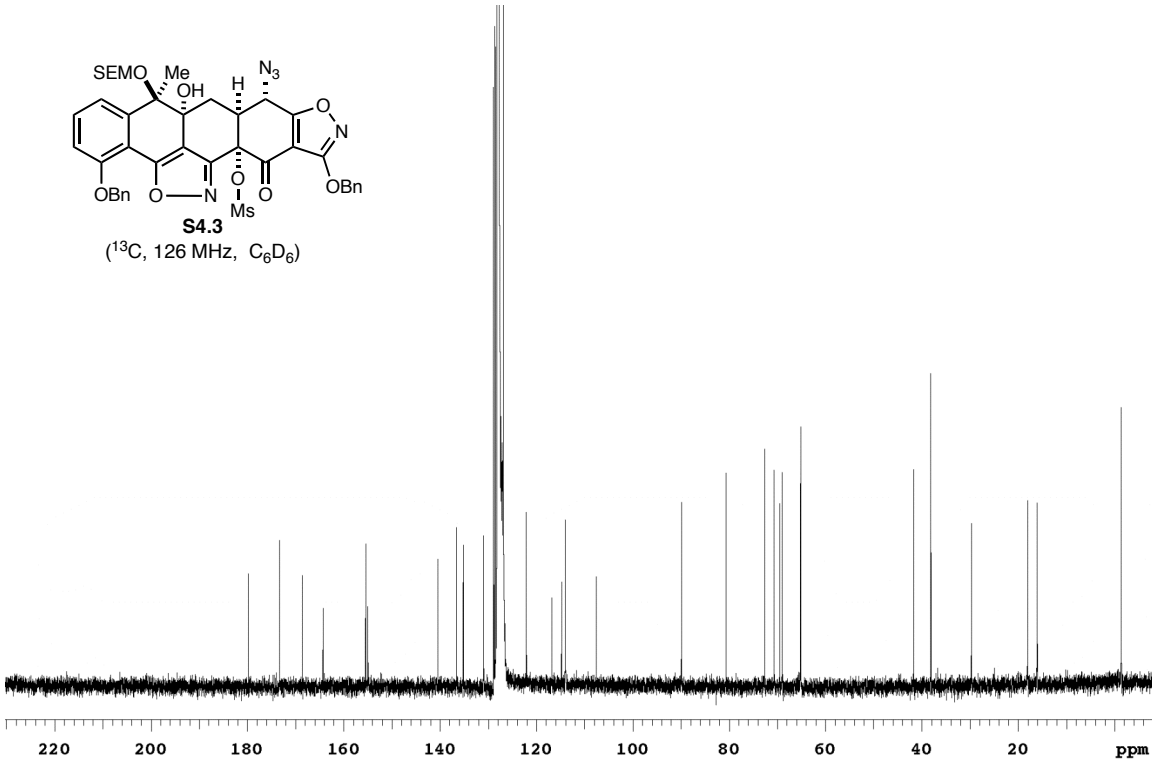
**4.24**

($^{13}$C, 126 MHz, $C_6D_6$)



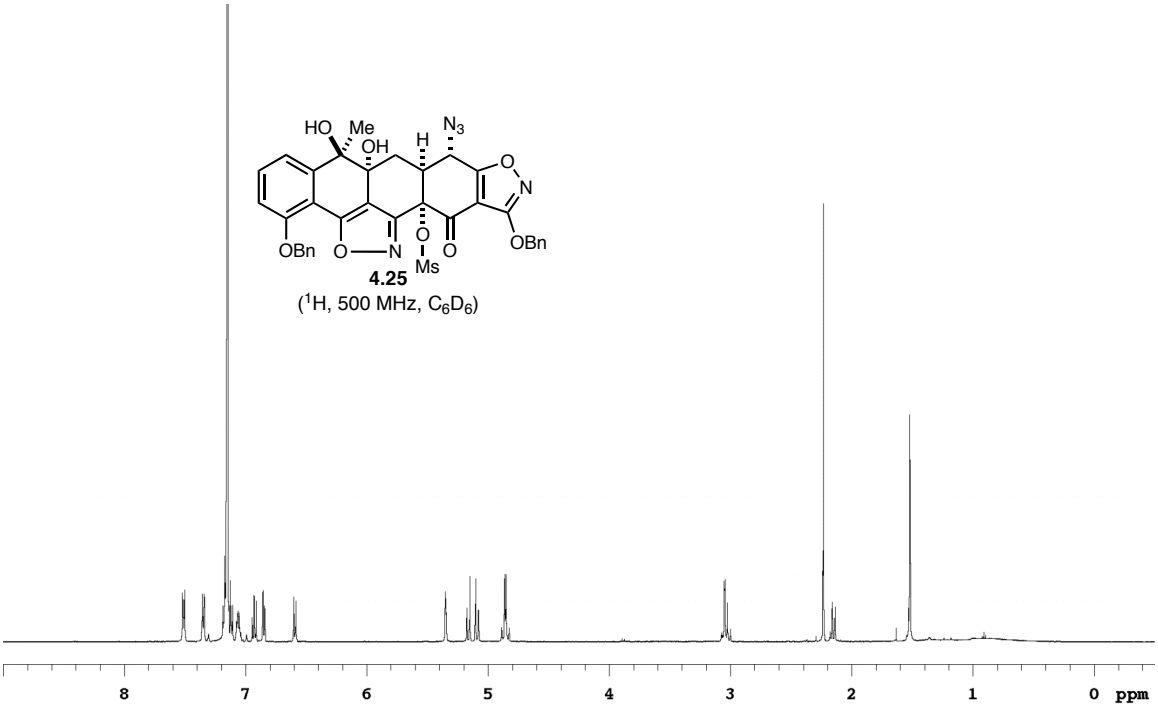

**S4.3**

($^1$H, 500 MHz, $C_6D_6$)



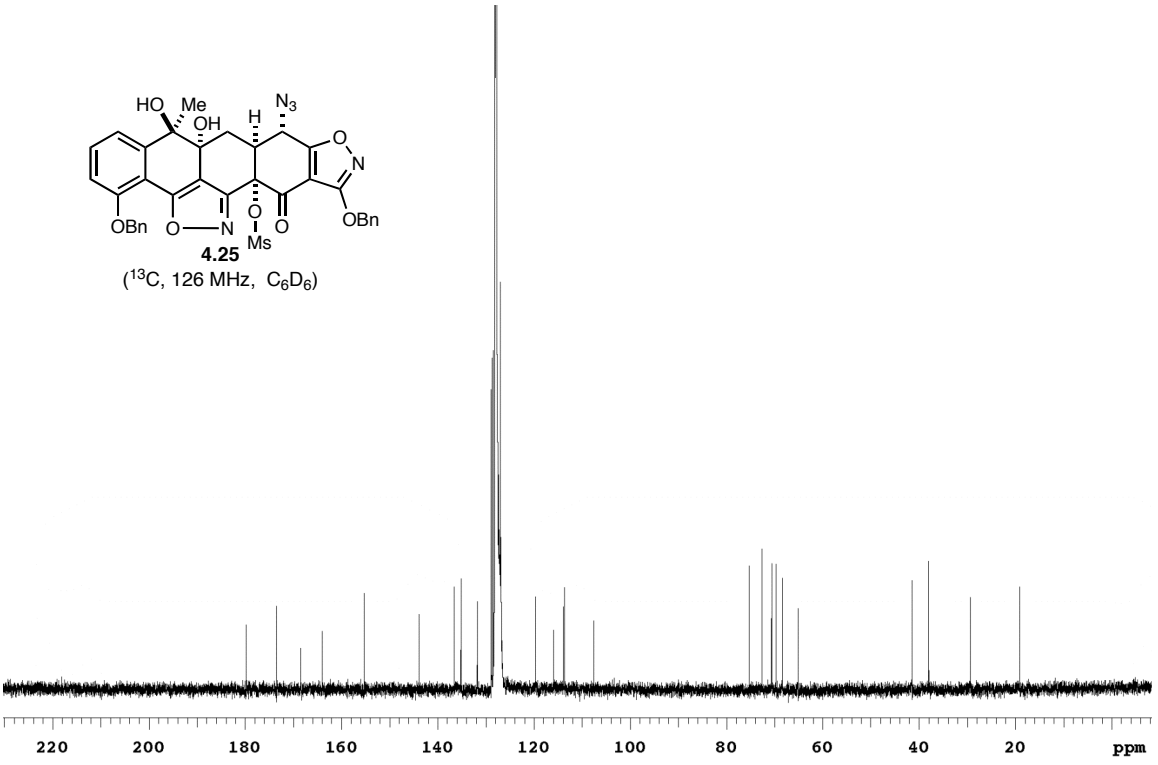

**S4.3**

($^{13}$C, 126 MHz, $C_6D_6$)



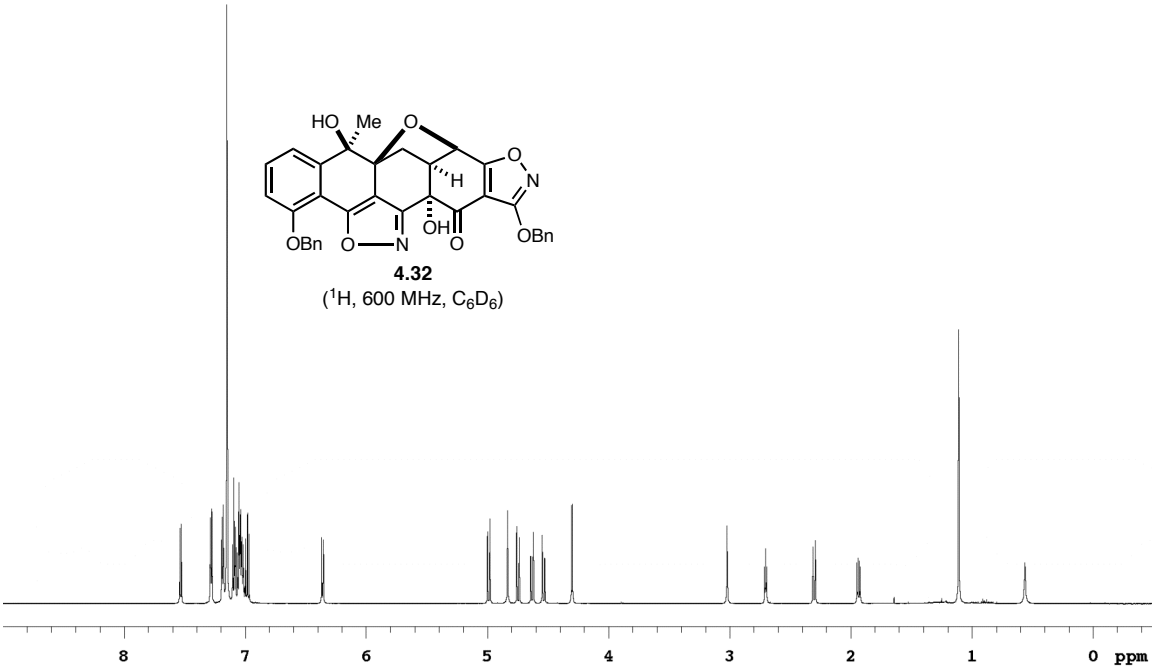

**4.25**

($^1$H, 500 MHz, $C_6D_6$)

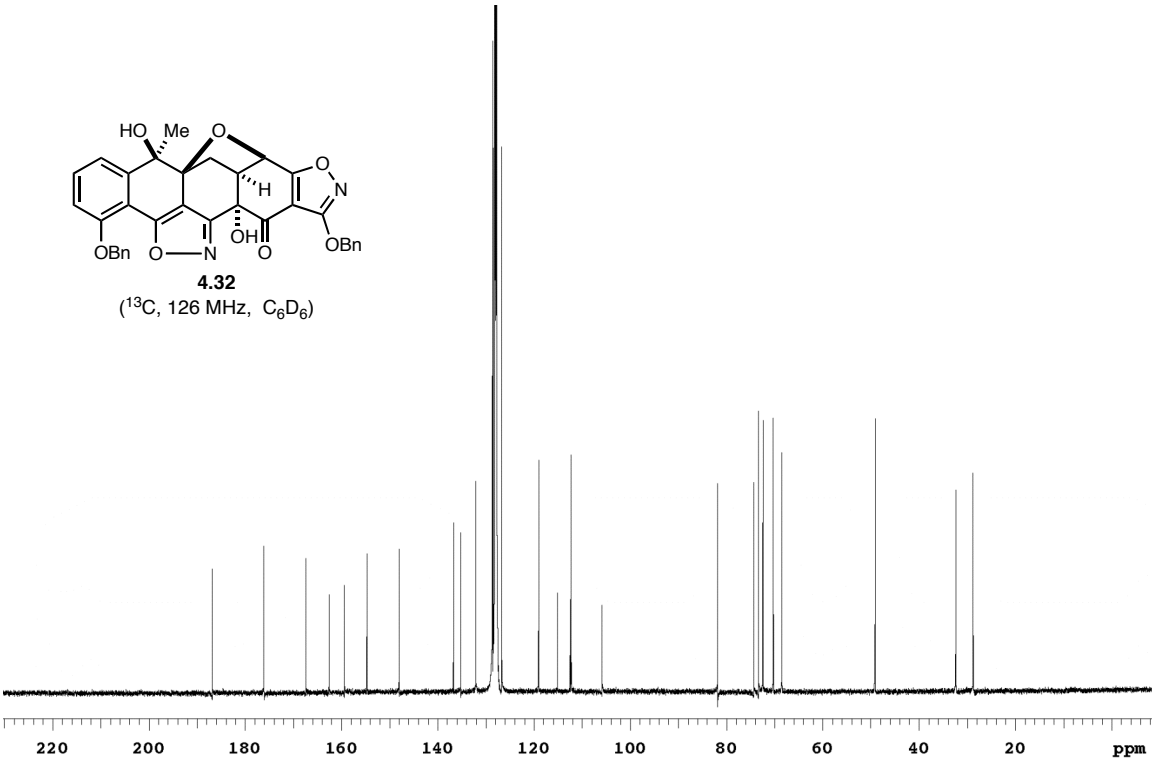



**4.25**

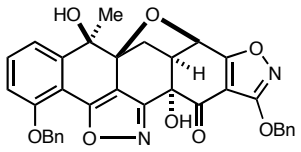
($^{13}$C, 126 MHz, $C_6D_6$)



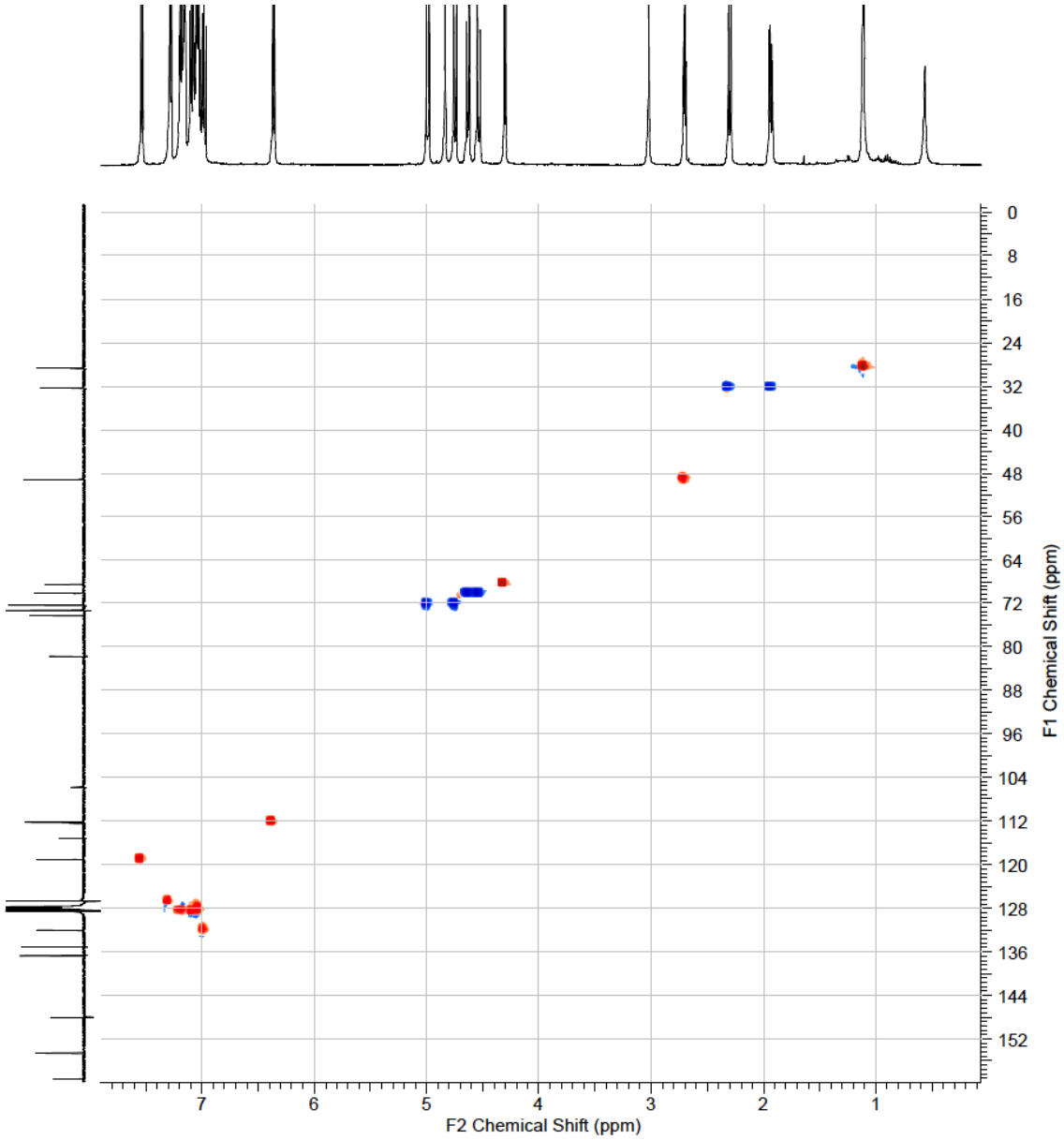

**4.32**
($^1$H, 600 MHz, $C_6D_6$)

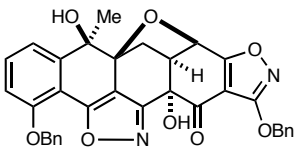



**4.32**
($^{13}$C, 126 MHz, $C_6D_6$)

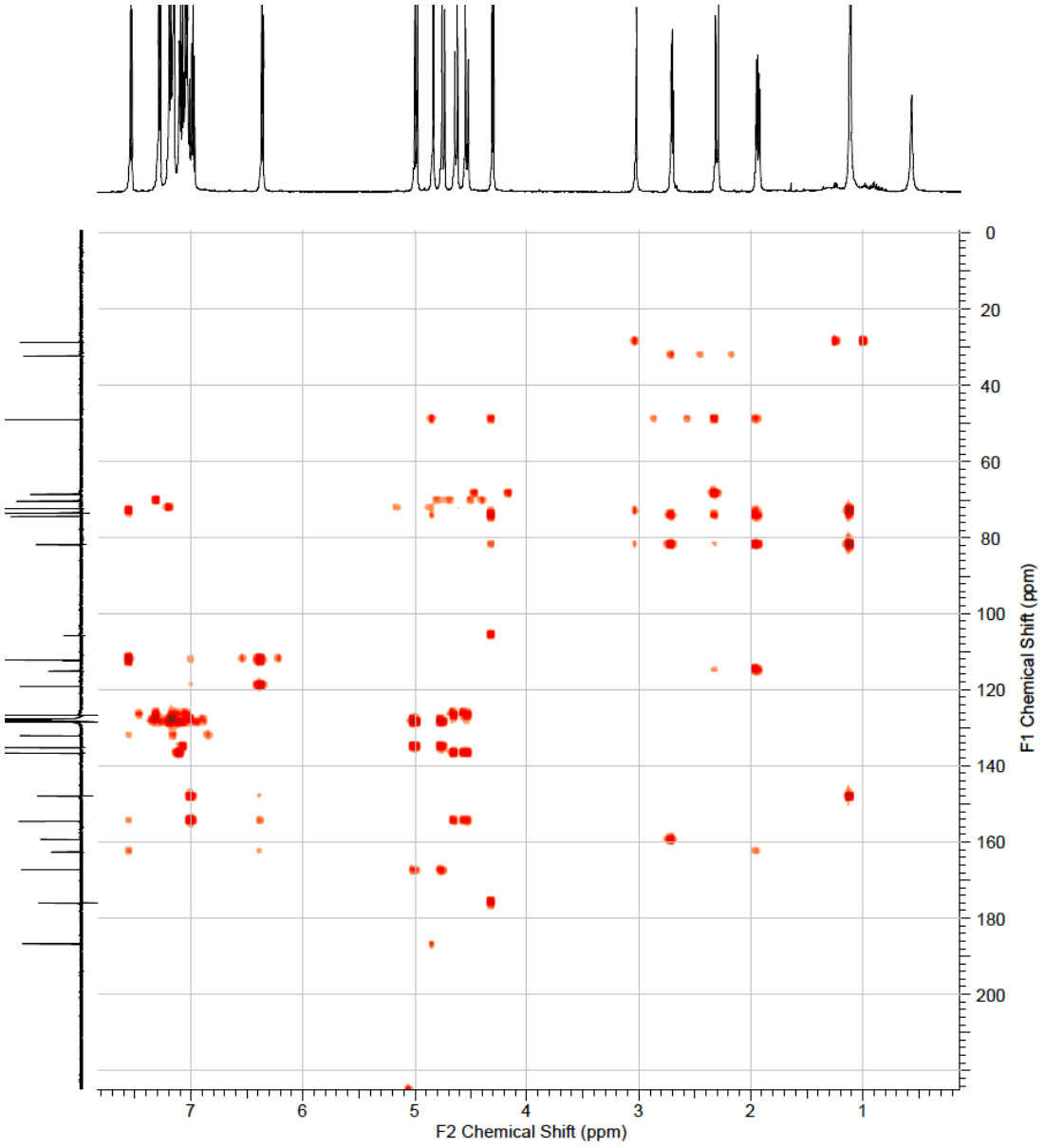


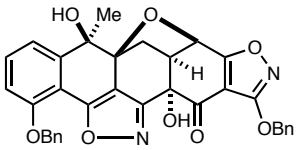

**4.32**
(HSQC, 500 MHz, C6D6)



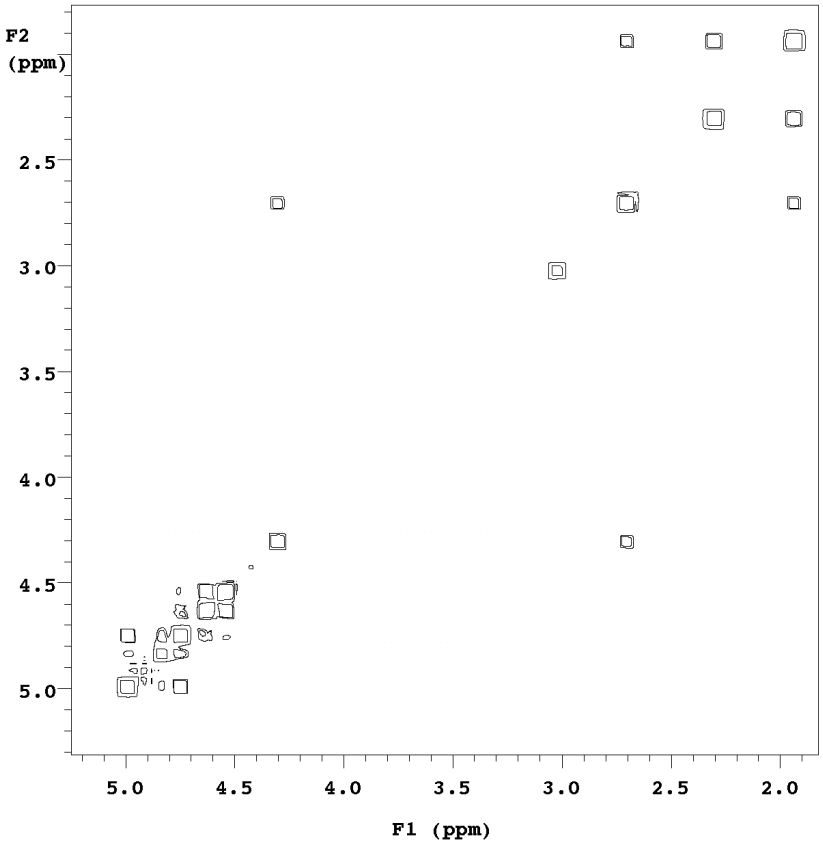


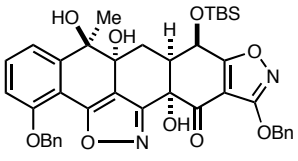

**4.32**
(HMBC, 500 MHz, C6D6)





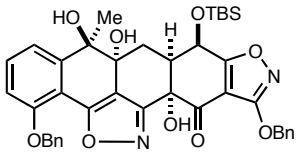

**4.32**
(COSY, 600 MHz, C6D6)



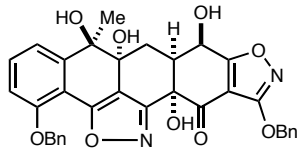



**S4.4**
($^1$H, 500 MHz, $C_6D_6$)



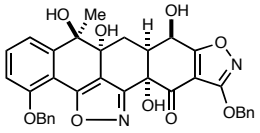

**S4.4**
($^{13}$C, 126 MHz, $C_6D_6$)




**4.37**

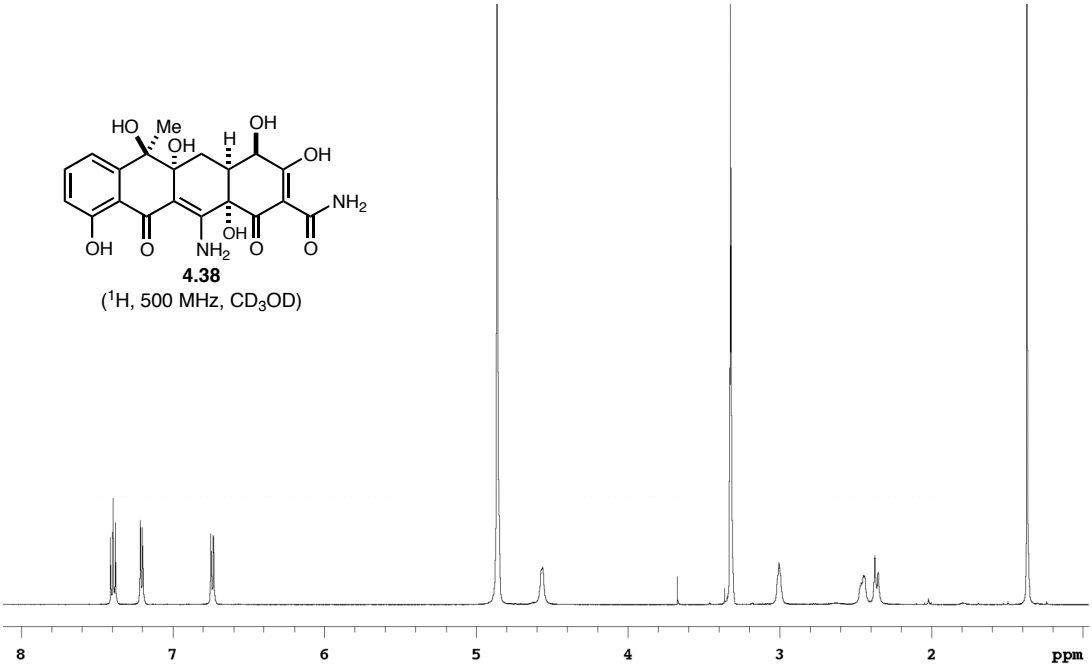
($^1$H, 600 MHz, $CD_3CN$)



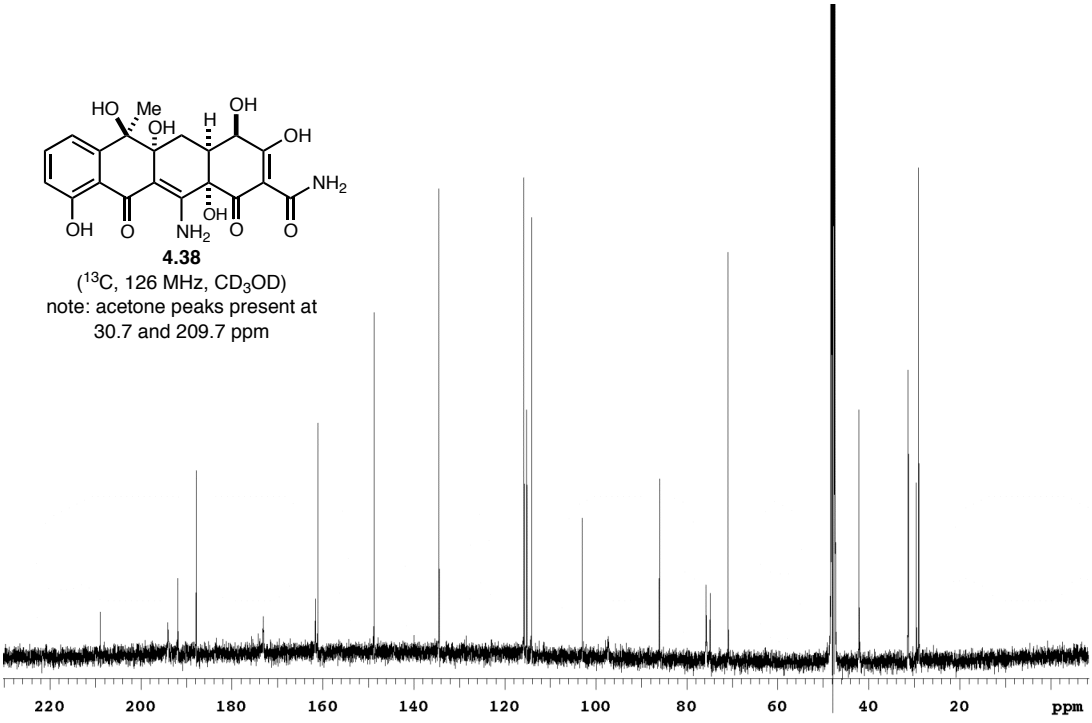

**4.37**

($^{13}$C, 126 MHz, $CD_3CN$)




**4.38**

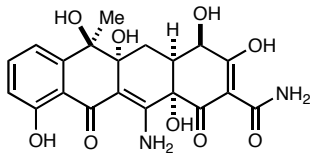
($^1$H, 500 MHz, $CD_3OD$)




**4.38**

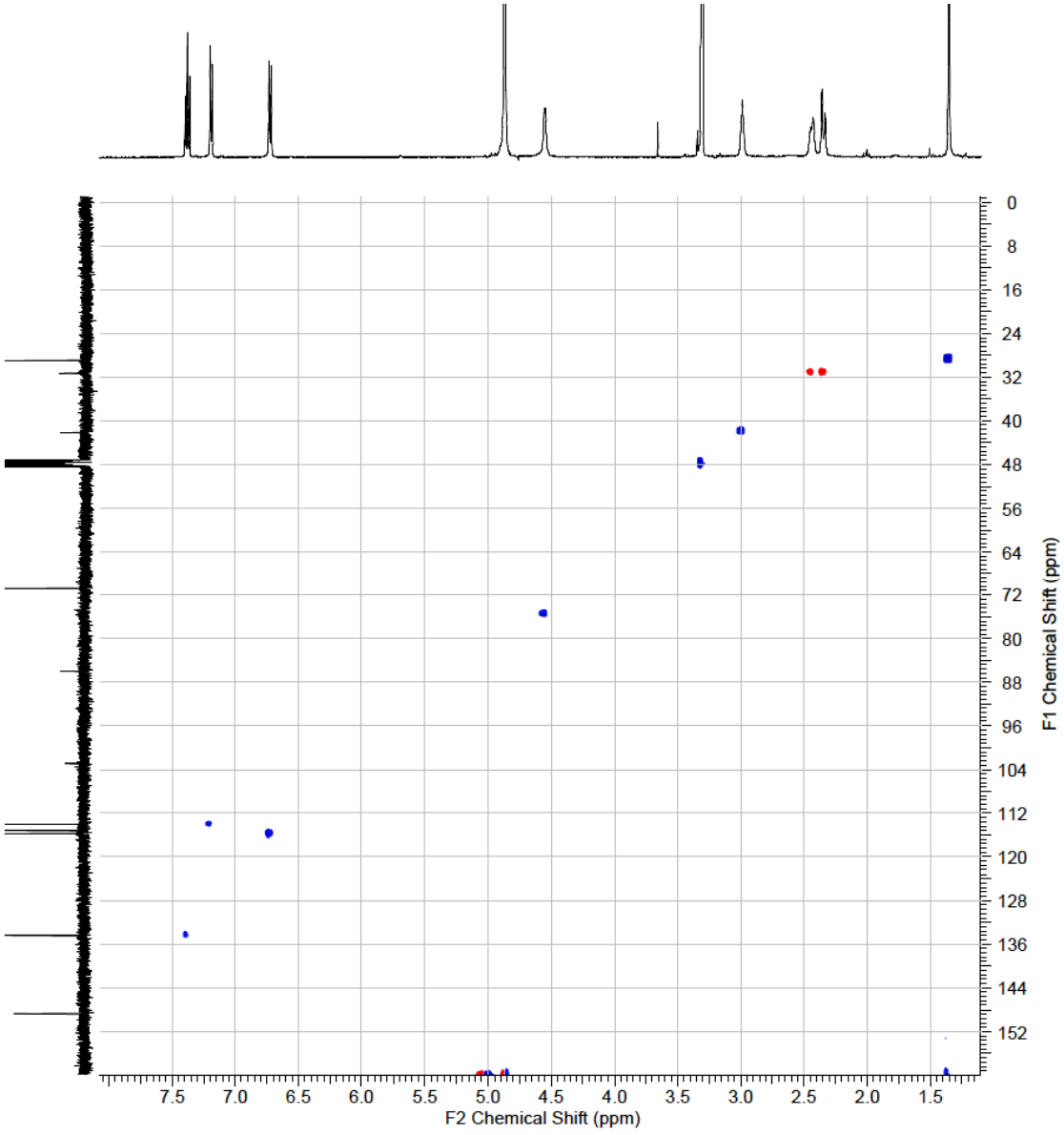
($^{13}$C, 126 MHz, $CD_3OD$)

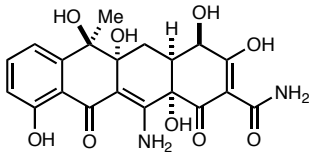
note: acetone peaks present at 30.7 and 209.7 ppm




**4.38**

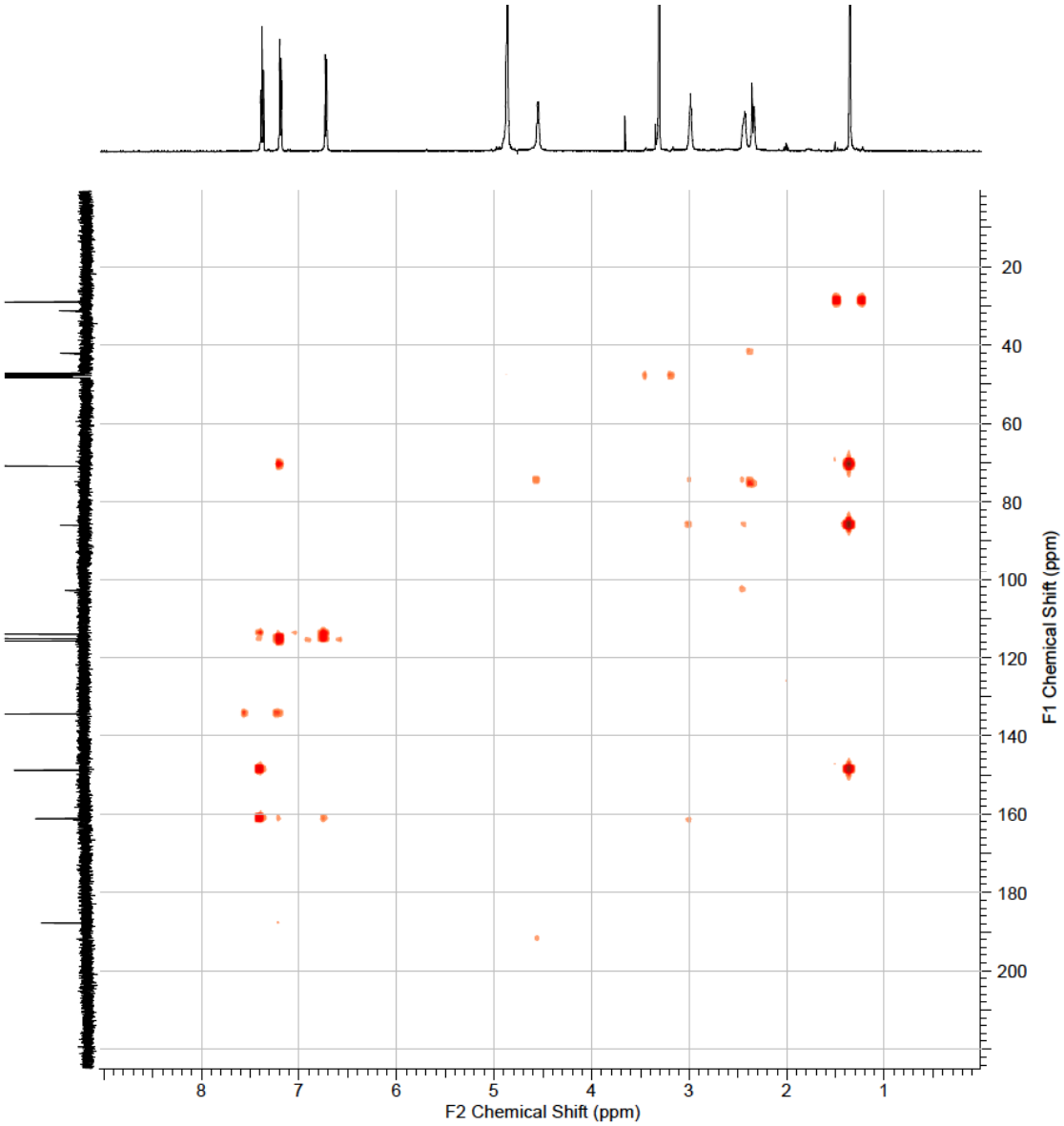
(HSQC, 500 MHz, $CD_3OD$)

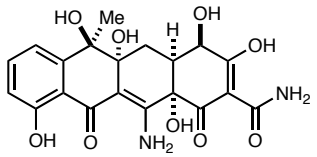





**4.38**

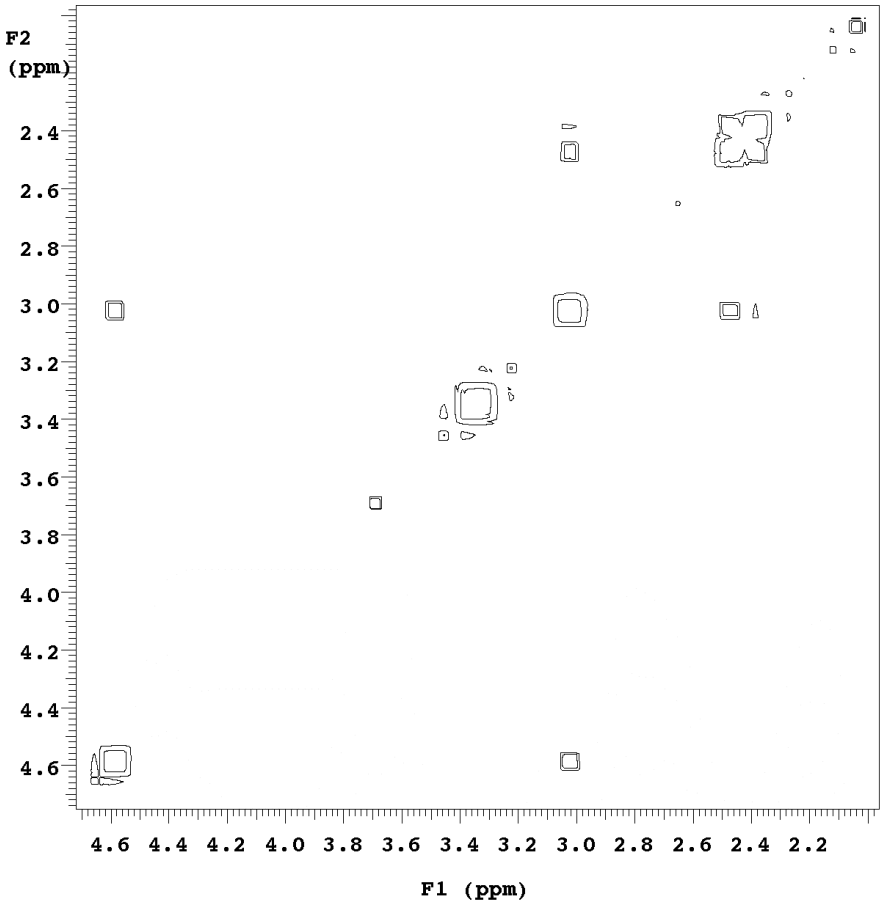
(HMBC, 500 MHz, $CD_3OD$)

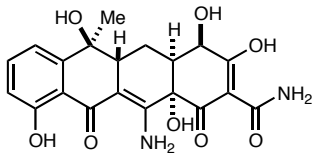





**4.38**

(COSY, 600 MHz, $CD_3OD$)

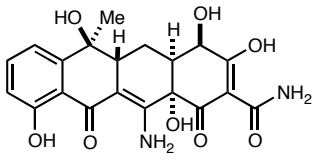





**4.44**

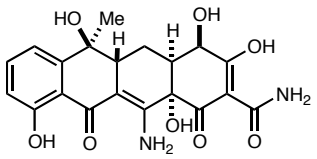
($^{1}$H, 600 MHz, $d_6$-DMSO)



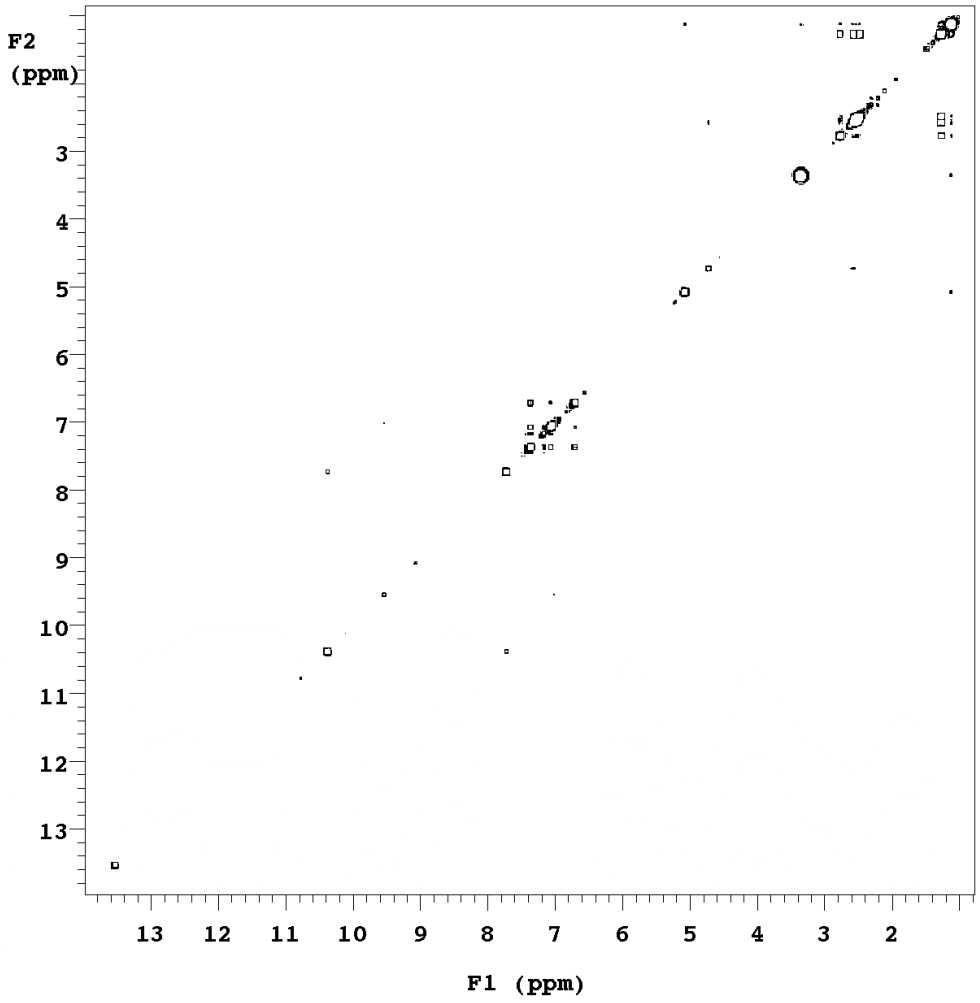

**4.44**

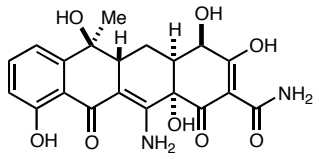
($^{13}$C, 126 MHz, $d_6$-DMSO)




**4.44**

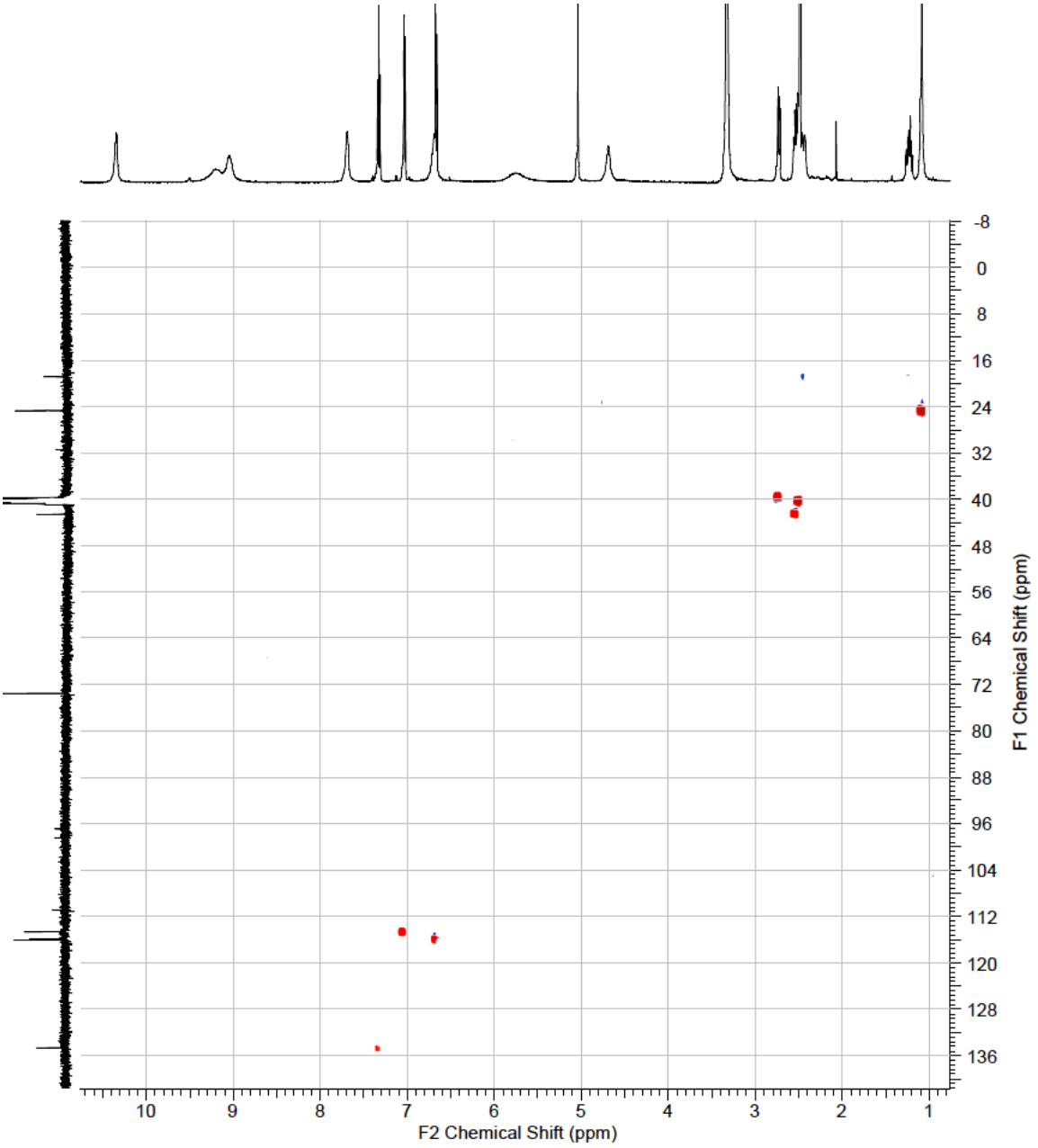
(COSY, 600 MHz, $d_6$-DMSO)

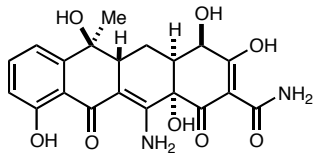





**4.44**

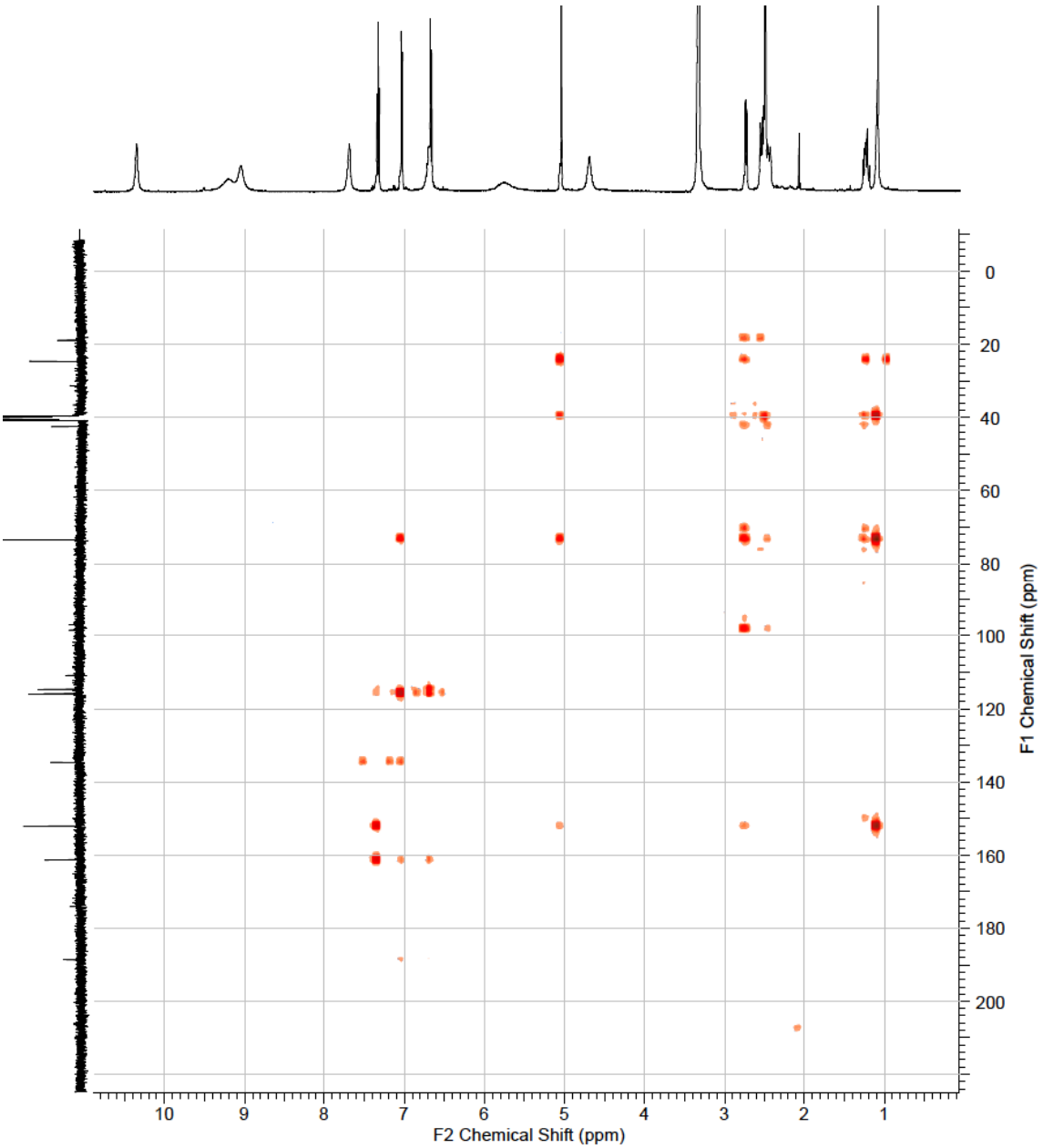
(HSQC, 500 MHz, $d_6$-DMSO)

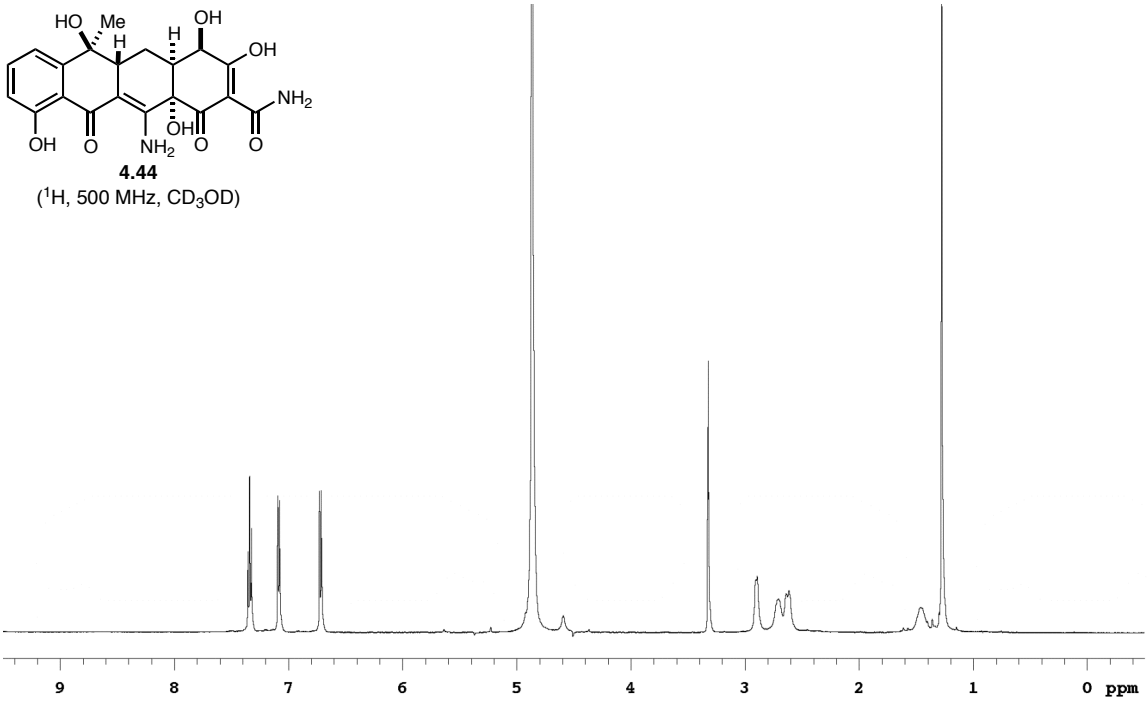





**4.44**

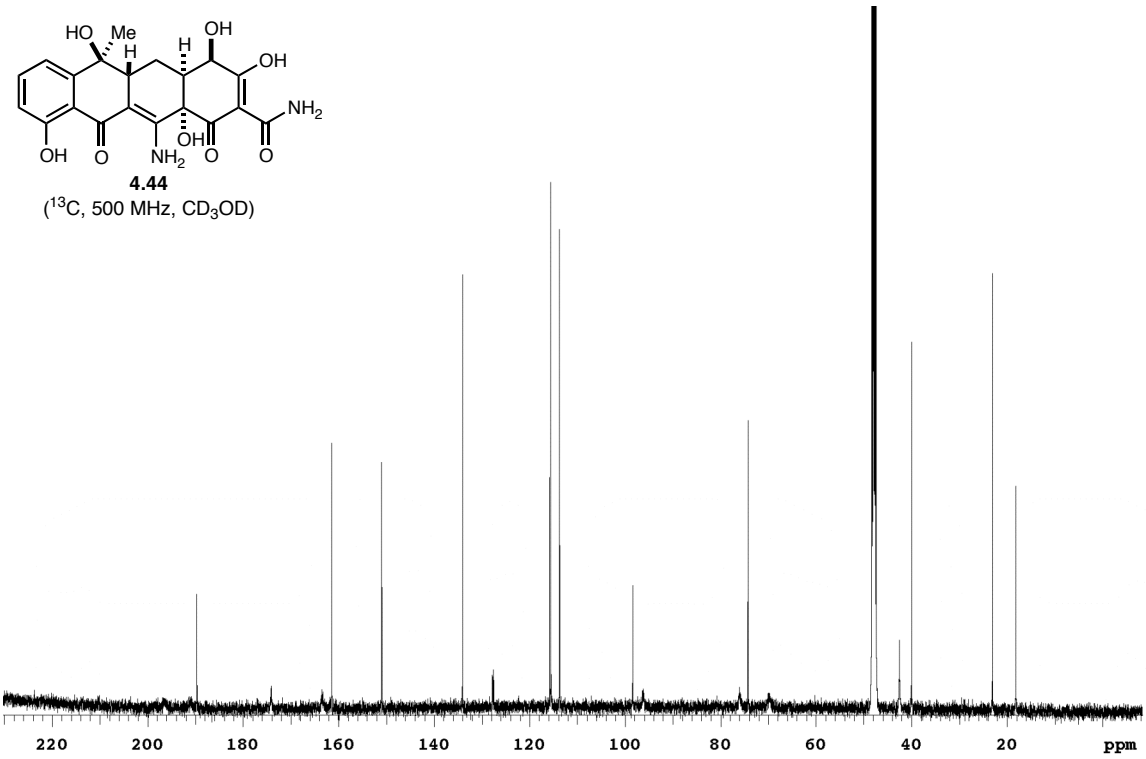
(HMBC, 500 MHz, $d_6$-DMSO)






**4.44**

($^{1}$H, 500 MHz, $CD_3OD$)



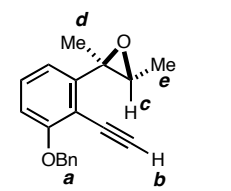

**4.44**

($^{13}$C, 500 MHz, $CD_3OD$)

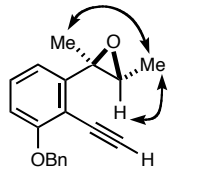
# *Appendix 2*

**Stereochemical Proofs**

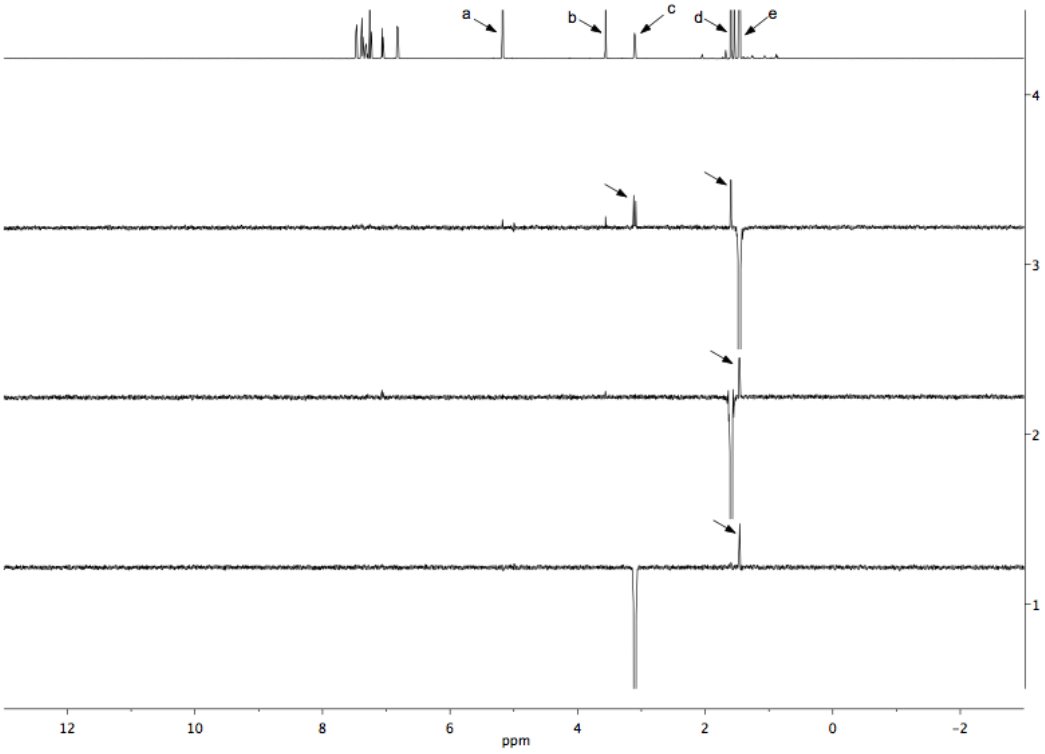
**Epoxide S2.2**: 1D-nOe Data



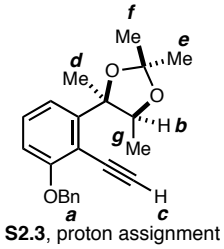

**S2.2**, proton assignment)



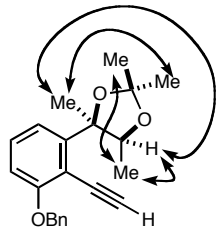

**S2.2**, compiled nOe data)
($^1$H, 500 MHz, $CDCl_3$)



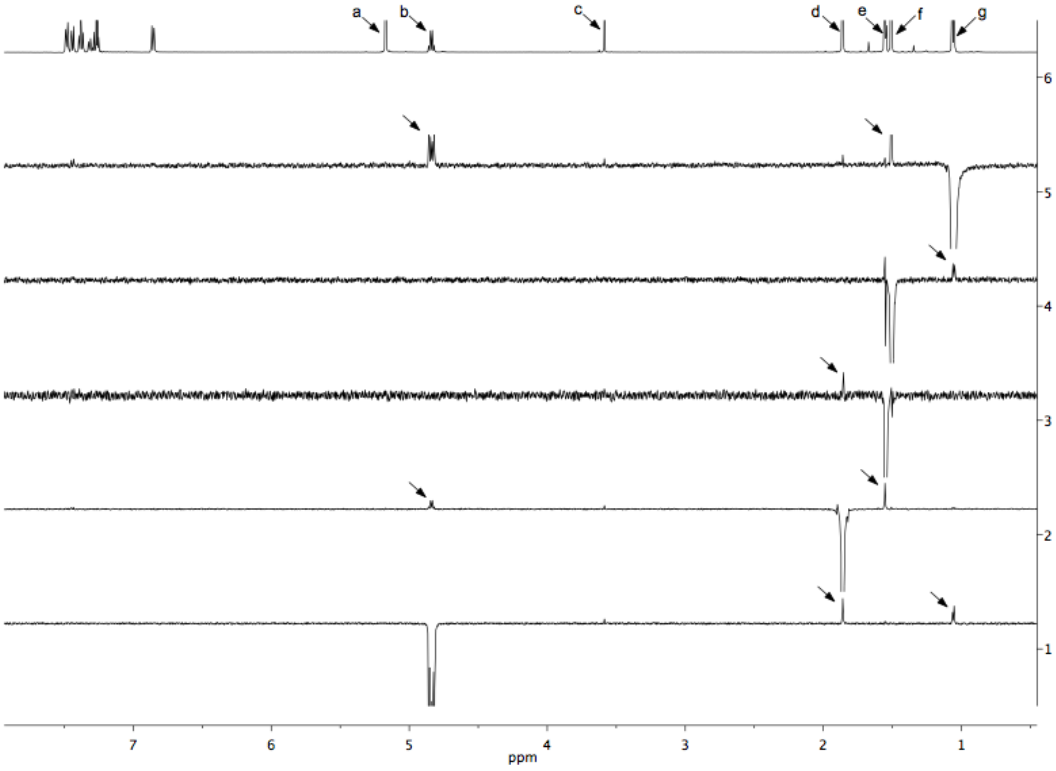
**Acetonide S2.3**: 1D-nOe Data



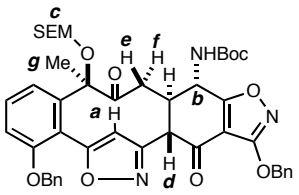

**S2.3**, proton assignment



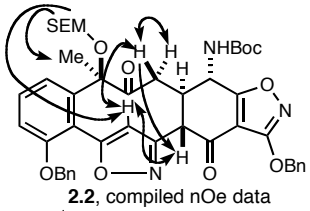

**S2.3**, compiled nOe data
($^1$H, 500 MHz, $CDCl_3$)



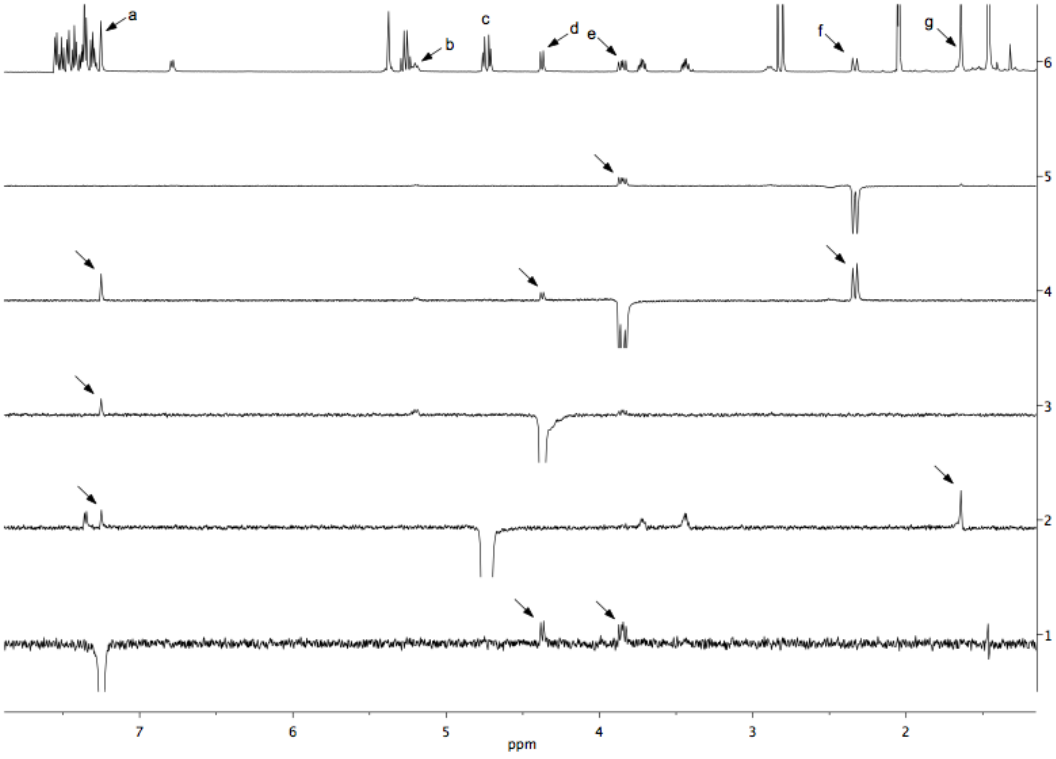
**Michael product 2.2**: 1D-nOe Data



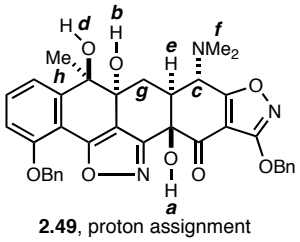

**2.2**, proton assignment



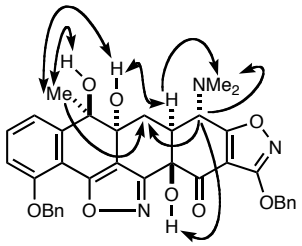

**2.2**, compiled nOe data
($^1$H, 600 MHz, acetone-$D_6$)



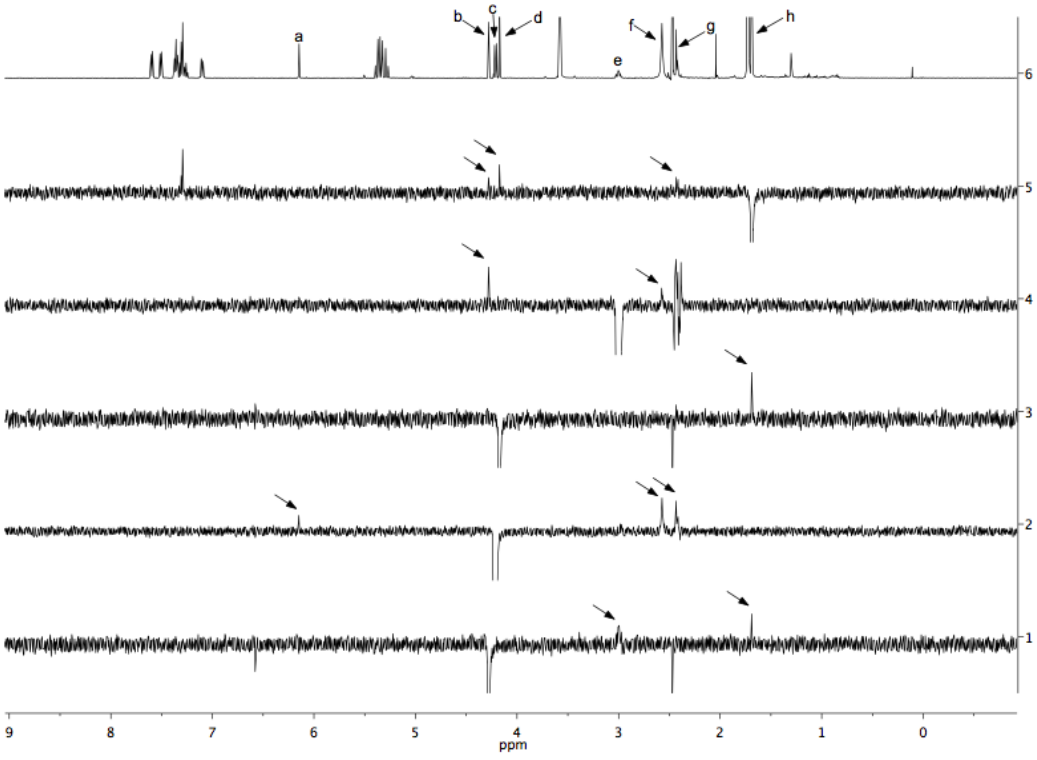
## **Dimethylamine 2.49**: 1D-nOe Data



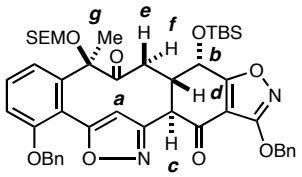

**2.49**, proton assignment



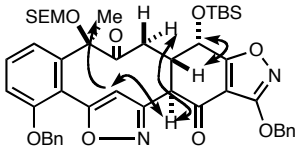

**2.49**, compiled nOe data
($^1$H, 500 MHz, THF-$D_8$)



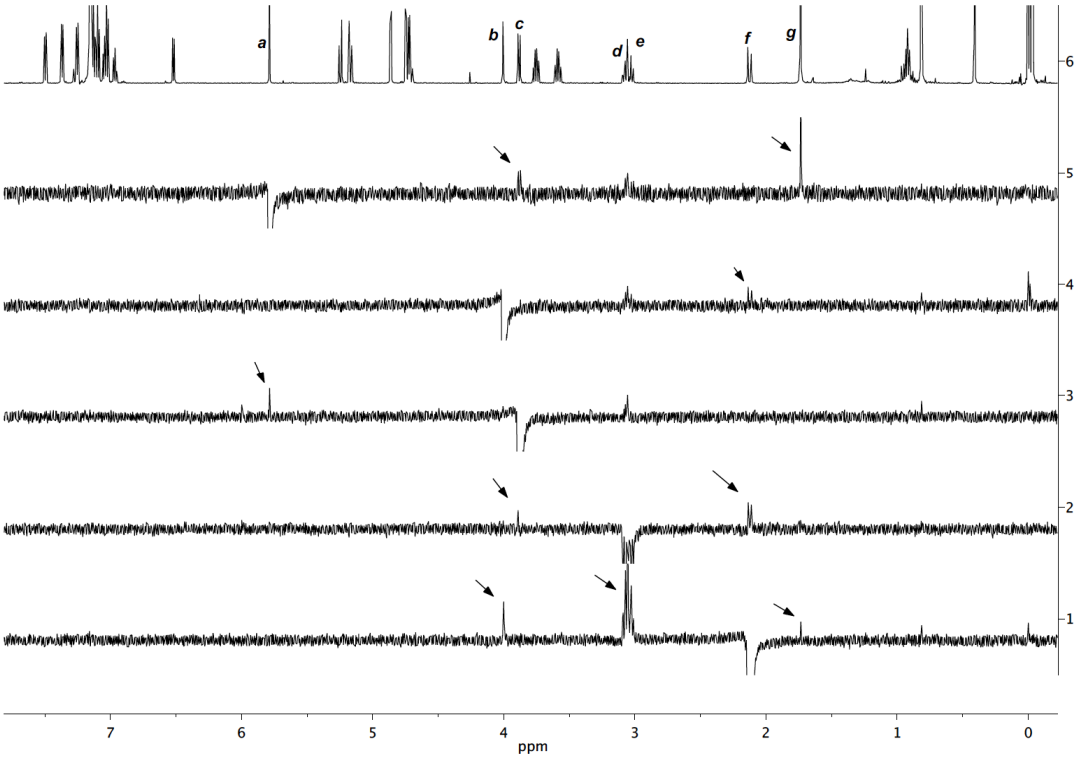
# **3.31**: 1D-nOe Data



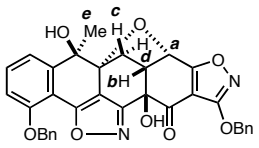

**3.31**, proton assignment



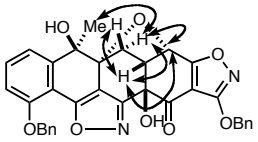

**3.31**, compiled nOe data
($^1$H, 600 MHz, C6D6)



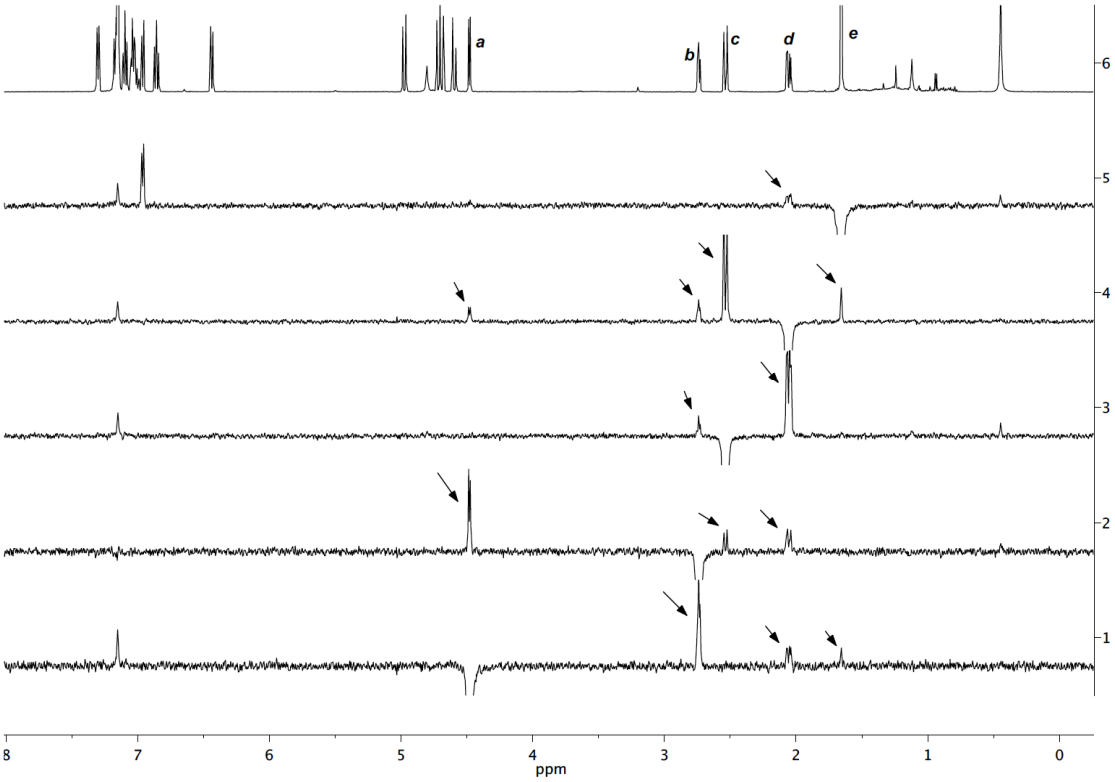
**3.55**: 1D-nOe Data



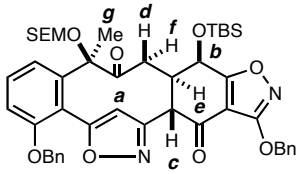

**3.55**, proton assignment



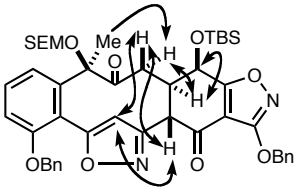

**3.55**, compiled nOe data
($^1$H, 500 MHz, C6D6)



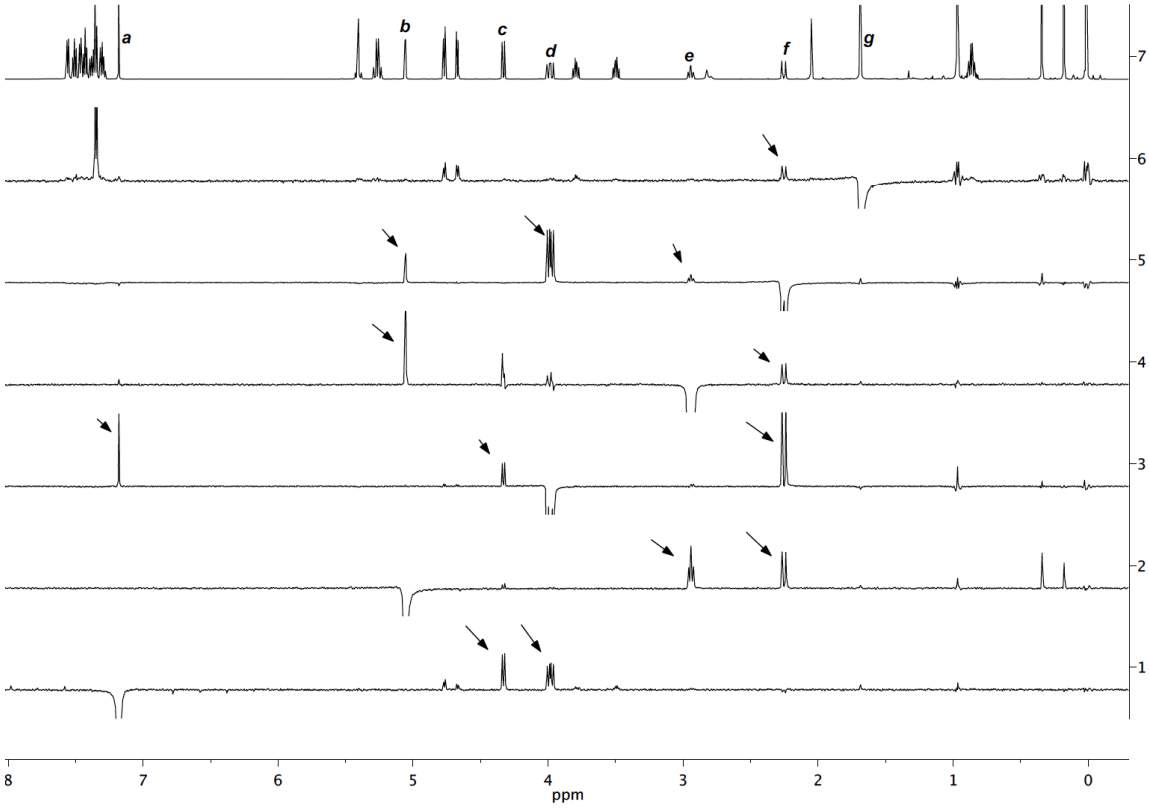
**4.9**: 1D-nOe Data



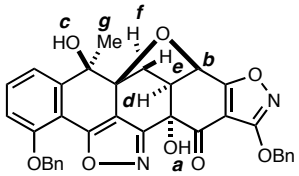

**4.9**, proton assignment



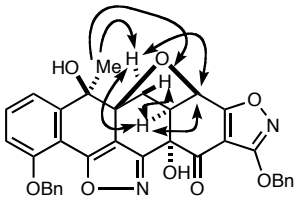

**4.9**, compiled nOe data
($^1$H, 600 MHz, C6D6)



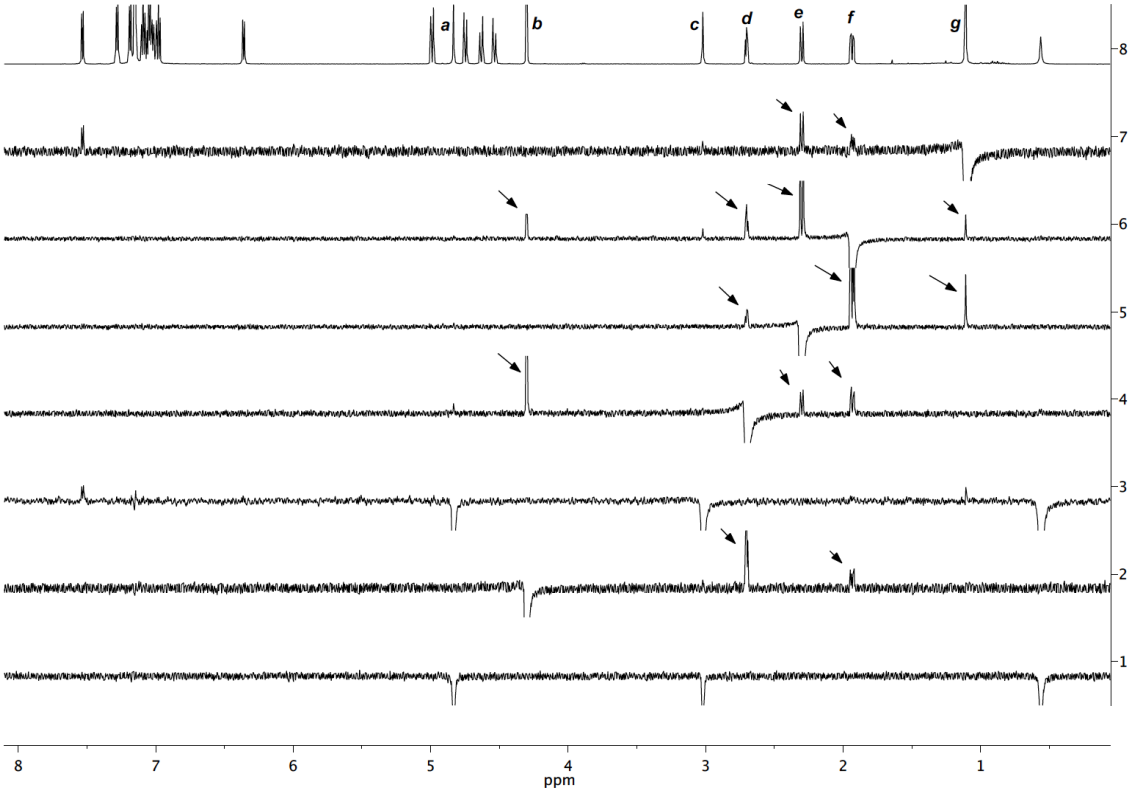
## **4.32**: 1D-nOe Data




**4.32**, proton assignment

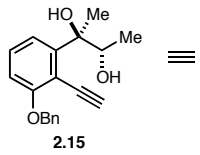



**4.32**, compiled nOe data
($^1$H, 500 MHz, C6D6)



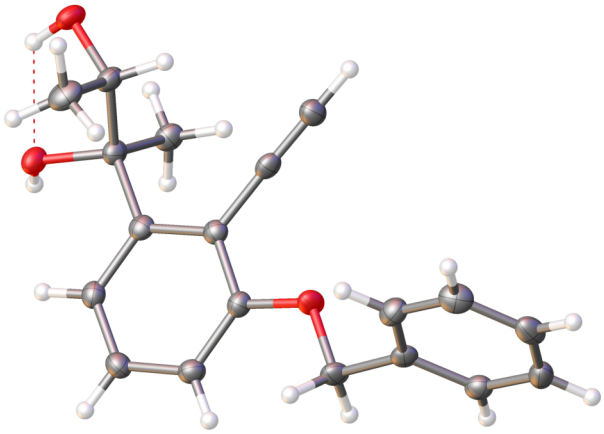
# *Appendix 3*

## Crystal Structure Data




**2.15**

≡



### I. X-Ray Crystallography

A crystal mounted on a diffractometer was collected data at 100 K. The intensities of the reflections were collected by means of a Bruker APEX II DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, λ=1.54178 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in $\omega$ at 30°, 55°, 80° and 105° in $2\theta$. Data integration down to 0.84 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods

again $F^2$ using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1, and geometric parameters are shown in Table 2, and hydrogen-bond parameters are list in Table 3. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

## II. Experimental details

| | |
|---|---|
| Sample name | JSW-1232 |
| Crystal data | |
| Chemical formula | $C_{38}H_{40}O_6$ |
| $M_r$ | 592.70 |
| Crystal system, space group | Triclinic, *P*1 |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 6.9527 (1), 8.9852 (2), 12.9087 (3) |
| α, β, γ (°) | 96.556 (1), 99.310 (1), 92.846 (1) |
| *V* (Å$^3$) | 788.69 (3) |
| *Z* | 1 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 0.67 |
| Crystal size (mm) | 0.24 × 0.20 × 0.16 |
| Data collection | |
| Diffractometer | Bruker D8 goniometer with CCD area detector diffractometer |
| Absorption correction | Multi-scan<br>*SADABS* |
| $T_{min}$, $T_{max}$ | 0.856, 0.901 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 19531, 4718, 4696 |
| $R_{int}$ | 0.028 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.025, 0.067, 1.06 |
| No. of reflections | 4718 |
| No. of parameters | 426 |
| No. of restraints | 3 |

| | |
|---|---|
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.18, -0.14 |
| Absolute structure | Flack H D (1983), Acta Cryst. A39, 876-881 |
| Flack parameter | 0.00 (10) |

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

## III. Selected geometric parameters (Å, º)

| | | | |
|---|---|---|---|
| O1—C1 | 1.3681 (16) | O4—C21 | 1.3714 (17) |
| O1—C7 | 1.4364 (16) | O4—C27 | 1.4406 (17) |
| O2—C14 | 1.4365 (15) | O5—C34 | 1.4471 (15) |
| O2—H2 | 0.89 (2) | O5—H5 | 0.88 (2) |
| O3—C15 | 1.4451 (17) | O6—C35 | 1.4401 (16) |
| O3—H3 | 0.90 (2) | O6—H6 | 0.89 (2) |
| C1—C2 | 1.3919 (19) | C21—C22 | 1.386 (2) |
| C1—C6 | 1.4107 (19) | C21—C26 | 1.4156 (19) |
| C2—C3 | 1.387 (2) | C22—C23 | 1.381 (2) |
| C2—H2A | 0.9500 | C22—H22 | 0.9500 |
| C3—C4 | 1.383 (2) | C23—C24 | 1.384 (2) |
| C3—H3A | 0.9500 | C23—H23 | 0.9500 |
| C4—C5 | 1.3962 (19) | C24—C25 | 1.3953 (19) |
| C4—H4 | 0.9500 | C24—H24 | 0.9500 |
| C5—C6 | 1.4140 (18) | C25—C26 | 1.4088 (19) |
| C5—C14 | 1.5352 (19) | C25—C34 | 1.5314 (19) |
| C6—C18 | 1.4379 (19) | C26—C38 | 1.4433 (19) |
| C7—C8 | 1.5006 (19) | C27—C28 | 1.4985 (19) |
| C7—H7A | 0.9900 | C27—H27A | 0.9900 |
| C7—H7B | 0.9900 | C27—H27B | 0.9900 |
| C8—C9 | 1.388 (2) | C28—C29 | 1.388 (2) |
| C8—C13 | 1.395 (2) | C28—C33 | 1.389 (2) |
| C9—C10 | 1.381 (2) | C29—C30 | 1.383 (2) |
| C9—H9 | 0.9500 | C29—H29 | 0.9500 |
| C10—C11 | 1.385 (2) | C30—C31 | 1.369 (3) |
| C10—H10 | 0.9500 | C30—H30 | 0.9500 |
| C11—C12 | 1.389 (2) | C31—C32 | 1.388 (3) |
| C11—H11 | 0.9500 | C31—H31 | 0.9500 |

| | | | |
|---|---|---|---|
| C12—C13 | 1.382 (2) | C32—C33 | 1.390 (2) |
| C12—H12 | 0.9500 | C32—H32 | 0.9500 |
| C13—H13 | 0.9500 | C33—H33 | 0.9500 |
| C14—C17 | 1.534 (2) | C34—C37 | 1.5253 (19) |
| C14—C15 | 1.5451 (18) | C34—C35 | 1.5583 (19) |
| C15—C16 | 1.517 (2) | C35—C36 | 1.511 (2) |
| C15—H15 | 1.0000 | C35—H35 | 1.0000 |
| C16—H16A | 0.9800 | C36—H36A | 0.9800 |
| C16—H16B | 0.9800 | C36—H36B | 0.9800 |
| C16—H16C | 0.9800 | C36—H36C | 0.9800 |
| C17—H17A | 0.9800 | C37—H37A | 0.9800 |
| C17—H17B | 0.9800 | C37—H37B | 0.9800 |
| C17—H17C | 0.9800 | C37—H37C | 0.9800 |
| C18—C19 | 1.189 (2) | C38—C39 | 1.185 (2) |
| C19—H19 | 0.970 (19) | C39—H39 | 0.90 (2) |
| | | | |
| C1—O1—C7 | 116.41 (10) | C21—O4—C27 | 115.60 (10) |
| C14—O2—H2 | 108.9 (12) | C34—O5—H5 | 103.5 (14) |
| C15—O3—H3 | 105.2 (14) | C35—O6—H6 | 109.7 (13) |
| O1—C1—C2 | 123.90 (12) | O4—C21—C22 | 123.80 (13) |
| O1—C1—C6 | 114.98 (11) | O4—C21—C26 | 115.21 (12) |
| C2—C1—C6 | 121.12 (12) | C22—C21—C26 | 120.98 (13) |
| C3—C2—C1 | 118.68 (13) | C23—C22—C21 | 118.94 (13) |
| C3—C2—H2A | 120.7 | C23—C22—H22 | 120.5 |
| C1—C2—H2A | 120.7 | C21—C22—H22 | 120.5 |
| C4—C3—C2 | 121.27 (12) | C22—C23—C24 | 121.13 (13) |
| C4—C3—H3A | 119.4 | C22—C23—H23 | 119.4 |
| C2—C3—H3A | 119.4 | C24—C23—H23 | 119.4 |
| C3—C4—C5 | 120.95 (12) | C23—C24—C25 | 121.00 (12) |
| C3—C4—H4 | 119.5 | C23—C24—H24 | 119.5 |
| C5—C4—H4 | 119.5 | C25—C24—H24 | 119.5 |
| C4—C5—C6 | 118.68 (13) | C24—C25—C26 | 118.65 (13) |
| C4—C5—C14 | 119.39 (11) | C24—C25—C34 | 119.70 (12) |
| C6—C5—C14 | 121.86 (11) | C26—C25—C34 | 121.44 (12) |
| C1—C6—C5 | 119.23 (12) | C25—C26—C21 | 119.17 (12) |
| C1—C6—C18 | 117.10 (12) | C25—C26—C38 | 123.40 (12) |
| C5—C6—C18 | 123.64 (12) | C21—C26—C38 | 117.43 (12) |
| O1—C7—C8 | 108.80 (10) | O4—C27—C28 | 108.83 (11) |

| | | | |
|---|---|---|---|
| O1—C7—H7A | 109.9 | O4—C27—H27A | 109.9 |
| C8—C7—H7A | 109.9 | C28—C27—H27A | 109.9 |
| O1—C7—H7B | 109.9 | O4—C27—H27B | 109.9 |
| C8—C7—H7B | 109.9 | C28—C27—H27B | 109.9 |
| H7A—C7—H7B | 108.3 | H27A—C27—H27B | 108.3 |
| C9—C8—C13 | 118.97 (13) | C29—C28—C33 | 119.29 (14) |
| C9—C8—C7 | 121.14 (12) | C29—C28—C27 | 120.56 (14) |
| C13—C8—C7 | 119.75 (12) | C33—C28—C27 | 120.14 (13) |
| C10—C9—C8 | 120.46 (13) | C30—C29—C28 | 120.19 (15) |
| C10—C9—H9 | 119.8 | C30—C29—H29 | 119.9 |
| C8—C9—H9 | 119.8 | C28—C29—H29 | 119.9 |
| C9—C10—C11 | 120.37 (13) | C31—C30—C29 | 120.41 (15) |
| C9—C10—H10 | 119.8 | C31—C30—H30 | 119.8 |
| C11—C10—H10 | 119.8 | C29—C30—H30 | 119.8 |
| C10—C11—C12 | 119.64 (14) | C30—C31—C32 | 120.31 (14) |
| C10—C11—H11 | 120.2 | C30—C31—H31 | 119.8 |
| C12—C11—H11 | 120.2 | C32—C31—H31 | 119.8 |
| C13—C12—C11 | 119.99 (14) | C31—C32—C33 | 119.50 (15) |
| C13—C12—H12 | 120.0 | C31—C32—H32 | 120.3 |
| C11—C12—H12 | 120.0 | C33—C32—H32 | 120.3 |
| C12—C13—C8 | 120.55 (13) | C28—C33—C32 | 120.29 (14) |
| C12—C13—H13 | 119.7 | C28—C33—H33 | 119.9 |
| C8—C13—H13 | 119.7 | C32—C33—H33 | 119.9 |
| O2—C14—C17 | 109.30 (11) | O5—C34—C37 | 107.82 (10) |
| O2—C14—C5 | 110.39 (10) | O5—C34—C25 | 106.82 (11) |
| C17—C14—C5 | 109.64 (11) | C37—C34—C25 | 109.95 (11) |
| O2—C14—C15 | 102.37 (10) | O5—C34—C35 | 106.17 (11) |
| C17—C14—C15 | 111.60 (11) | C37—C34—C35 | 111.02 (11) |
| C5—C14—C15 | 113.31 (11) | C25—C34—C35 | 114.69 (11) |
| O3—C15—C16 | 110.34 (11) | O6—C35—C36 | 106.53 (11) |
| O3—C15—C14 | 107.41 (11) | O6—C35—C34 | 107.70 (10) |
| C16—C15—C14 | 113.02 (11) | C36—C35—C34 | 114.74 (11) |
| O3—C15—H15 | 108.7 | O6—C35—H35 | 109.2 |
| C16—C15—H15 | 108.7 | C36—C35—H35 | 109.2 |
| C14—C15—H15 | 108.7 | C34—C35—H35 | 109.2 |
| C15—C16—H16A | 109.5 | C35—C36—H36A | 109.5 |
| C15—C16—H16B | 109.5 | C35—C36—H36B | 109.5 |
| H16A—C16—H16B | 109.5 | H36A—C36—H36B | 109.5 |

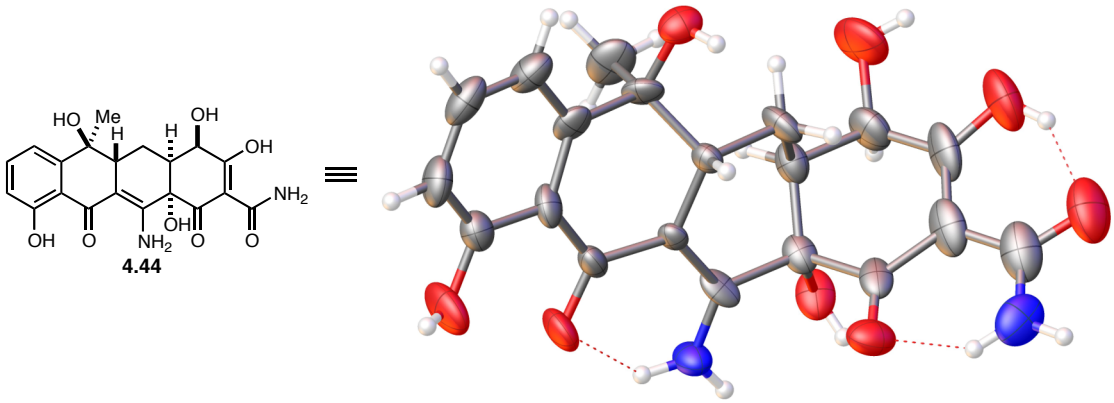
| | | | |
|---|---|---|---|
| C15—C16—H16C | 109.5 | C35—C36—H36C | 109.5 |
| H16A—C16—H16C | 109.5 | H36A—C36—H36C | 109.5 |
| H16B—C16—H16C | 109.5 | H36B—C36—H36C | 109.5 |
| C14—C17—H17A | 109.5 | C34—C37—H37A | 109.5 |
| C14—C17—H17B | 109.5 | C34—C37—H37B | 109.5 |
| H17A—C17—H17B | 109.5 | H37A—C37—H37B | 109.5 |
| C14—C17—H17C | 109.5 | C34—C37—H37C | 109.5 |
| H17A—C17—H17C | 109.5 | H37A—C37—H37C | 109.5 |
| H17B—C17—H17C | 109.5 | H37B—C37—H37C | 109.5 |
| C19—C18—C6 | 177.23 (15) | C39—C38—C26 | 178.24 (16) |
| C18—C19—H19 | 179.2 (11) | C38—C39—H39 | 177.5 (14) |
| | | | |
| C7—O1—C1—C2 | -3.42 (18) | C27—O4—C21—C22 | 11.80 (19) |
| C7—O1—C1—C6 | 176.49 (11) | C27—O4—C21—C26 | -167.17 (11) |
| O1—C1—C2—C3 | 177.03 (12) | O4—C21—C22—C23 | -175.58 (12) |
| C6—C1—C2—C3 | -2.87 (19) | C26—C21—C22—C23 | 3.3 (2) |
| C1—C2—C3—C4 | 2.0 (2) | C21—C22—C23—C24 | -0.6 (2) |
| C2—C3—C4—C5 | 0.5 (2) | C22—C23—C24—C25 | -2.3 (2) |
| C3—C4—C5—C6 | -2.18 (18) | C23—C24—C25—C26 | 2.3 (2) |
| C3—C4—C5—C14 | 174.91 (12) | C23—C24—C25—C34 | 177.18 (13) |
| O1—C1—C6—C5 | -178.68 (11) | C24—C25—C26—C21 | 0.44 (19) |
| C2—C1—C6—C5 | 1.23 (18) | C34—C25—C26—C21 | -174.35 (12) |
| O1—C1—C6—C18 | -0.41 (17) | C24—C25—C26—C38 | 179.90 (12) |
| C2—C1—C6—C18 | 179.50 (13) | C34—C25—C26—C38 | 5.12 (19) |
| C4—C5—C6—C1 | 1.29 (17) | O4—C21—C26—C25 | 175.72 (11) |
| C14—C5—C6—C1 | -175.72 (12) | C22—C21—C26—C25 | -3.28 (19) |
| C4—C5—C6—C18 | -176.85 (13) | O4—C21—C26—C38 | -3.78 (17) |
| C14—C5—C6—C18 | 6.13 (19) | C22—C21—C26—C38 | 177.22 (12) |
| C1—O1—C7—C8 | -167.88 (11) | C21—O4—C27—C28 | 161.08 (11) |
| O1—C7—C8—C9 | -113.01 (14) | O4—C27—C28—C29 | 99.27 (15) |
| O1—C7—C8—C13 | 71.35 (15) | O4—C27—C28—C33 | -81.49 (16) |
| C13—C8—C9—C10 | 0.2 (2) | C33—C28—C29—C30 | 0.3 (2) |
| C7—C8—C9—C10 | -175.52 (12) | C27—C28—C29—C30 | 179.57 (13) |
| C8—C9—C10—C11 | -0.6 (2) | C28—C29—C30—C31 | -0.8 (2) |
| C9—C10—C11—C12 | 0.1 (2) | C29—C30—C31—C32 | 0.6 (2) |
| C10—C11—C12—C13 | 0.9 (2) | C30—C31—C32—C33 | 0.1 (2) |
| C11—C12—C13—C8 | -1.4 (2) | C29—C28—C33—C32 | 0.3 (2) |
| C9—C8—C13—C12 | 0.9 (2) | C27—C28—C33—C32 | -178.96 (13) |

| | | | |
|---|---|---|---|
| C7—C8—C13—C12 | 176.60 (13) | C31—C32—C33—C28 | -0.5 (2) |
| C4—C5—C14—O2 | 9.43 (16) | C24—C25—C34—O5 | 8.22 (16) |
| C6—C5—C14—O2 | -173.57 (11) | C26—C25—C34—O5 | -177.05 (11) |
| C4—C5—C14—C17 | -111.03 (13) | C24—C25—C34—C37 | -108.51 (14) |
| C6—C5—C14—C17 | 65.97 (15) | C26—C25—C34—C37 | 66.22 (15) |
| C4—C5—C14—C15 | 123.57 (12) | C24—C25—C34—C35 | 125.55 (13) |
| C6—C5—C14—C15 | -59.44 (15) | C26—C25—C34—C35 | -59.72 (16) |
| O2—C14—C15—O3 | -51.13 (12) | O5—C34—C35—O6 | -40.00 (13) |
| C17—C14—C15—O3 | 65.65 (14) | C37—C34—C35—O6 | 76.92 (13) |
| C5—C14—C15—O3 | -170.00 (10) | C25—C34—C35—O6 | -157.71 (11) |
| O2—C14—C15—C16 | 70.81 (14) | O5—C34—C35—C36 | 78.41 (13) |
| C17—C14—C15—C16 | -172.41 (12) | C37—C34—C35—C36 | -164.67 (12) |
| C5—C14—C15—C16 | -48.06 (15) | C25—C34—C35—C36 | -39.29 (16) |

## IV. Hydrogen-bond parameters

| *D*—H···*A* | *D*—H (Å) | H···*A* (Å) | *D*···*A* (Å) | *D*—H···*A* (°) |
|---|---|---|---|---|
| O2—H2···O5$^{i}$ | 0.89 (2) | 1.87 (2) | 2.7466 (14) | 169.0 (18) |
| O6—H6···O3$^{ii}$ | 0.89 (2) | 1.87 (2) | 2.7372 (14) | 165.3 (19) |
| O3—H3···O2 | 0.90 (2) | 2.02 (2) | 2.5814 (14) | 119.8 (18) |
| O5—H5···O6 | 0.88 (2) | 1.99 (2) | 2.5784 (14) | 123.4 (17) |

Symmetry code(s): (i) *x*+1, *y*+1, *z*+1; (ii) *x*-1, *y*, *z*-1.




## V. X-Ray Crystallography

A crystal mounted on a diffractometer was collected data at 180 K. The intensities of the reflections were collected by means of a Bruker APEX II DUO CCD diffractometer ($Cu_{K\alpha}$ radiation, λ=1.54178 Å), and equipped with an Oxford Cryosystems nitrogen flow apparatus. The collection method involved 1.0° scans in $\omega$ at 30°, 55°, 80° and 115° in $2\theta$. Data integration down to 0.84 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods again $F^2$ using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1, geometric parameters are shown in Table 2, and hydrogen-bond parameters are listed in Table 3. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

## VI. Experimental Details

| | JSW-1547 |
|---|---|
| Crystal data | |
| Chemical formula | $C_{20}H_{20}N_2O_8$ |
| $M_r$ | 416.38 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 100 |
| $a$, $b$, $c$ (Å) | 7.1664 (2), 9.7435 (3), 25.4422 (6) |
| $V$ (Å$^3$) | 1776.52 (8) |
| $Z$ | 4 |
| Radiation type | Cu $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 1.03 |
| Crystal size (mm) | 0.20 × 0.14 × 0.12 |
| Data collection | |
| Diffractometer | Bruker D8 goniometer with CCD area detector diffractometer |
| Absorption correction | Multi-scan<br>*SADABS* |
| $T_{min}$, $T_{max}$ | 0.820, 0.886 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 21791, 3082, 2960 |
| $R_{int}$ | 0.061 |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.592 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.102, 0.244, 1.07 |
| No. of reflections | 3082 |
| No. of parameters | 359 |
| No. of restraints | 93 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.54, -0.34 |
| Absolute structure | Flack H D (1983), Acta Cryst. A39, 876-881 |
| Flack parameter | -0.8 (7) |

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL* (Sheldrick, 2008).

## VII. Geometric parameters (Å, º)

| | | | |
|---|---|---|---|
| C1—O1 | 1.440 (12) | O8—H8 | 0.8400 |
| C1—C2 | 1.469 (15) | C1A—O1A | 1.43 (2) |
| C1—C18 | 1.530 (9) | C1A—C2A | 1.46 (2) |
| C1—H1 | 1.0000 | C1A—C18A | 1.517 (18) |
| C2—O2 | 1.282 (10) | C1A—H1AA | 1.0000 |
| C2—C3 | 1.442 (17) | C2A—O2A | 1.308 (19) |
| C3—C19 | 1.407 (16) | C2A—C3A | 1.44 (2) |
| C3—C4 | 1.444 (12) | C3A—C19A | 1.41 (2) |
| C4—O4 | 1.219 (11) | C3A—C4A | 1.43 (2) |
| C4—C5 | 1.557 (11) | C4A—O4A | 1.20 (2) |
| C5—O5 | 1.445 (11) | C4A—C5A | 1.555 (19) |
| C5—C18 | 1.502 (10) | C5A—C18A | 1.485 (18) |
| C5—C6 | 1.546 (9) | C5A—C6A | 1.536 (17) |
| C6—N2 | 1.325 (10) | C6A—N2A | 1.324 (19) |
| C6—C7 | 1.381 (10) | C6A—C7A | 1.380 (19) |
| C7—C8 | 1.454 (8) | C7A—C8A | 1.446 (16) |
| C7—C16 | 1.514 (9) | C7A—C16A | 1.502 (17) |
| C8—O6 | 1.264 (9) | C8A—O6A | 1.256 (19) |
| C8—C9 | 1.479 (11) | C8A—C9A | 1.47 (2) |
| C9—C14 | 1.409 (11) | C9A—C14A | 1.41 (2) |
| C9—C10 | 1.415 (9) | C9A—C10A | 1.414 (18) |
| C10—C11 | 1.367 (13) | C10A—C11A | 1.37 (2) |
| C10—O7 | 1.371 (11) | C10A—O7A | 1.38 (2) |
| C11—C12 | 1.405 (14) | C11A—C12A | 1.41 (2) |
| C11—H11 | 0.9500 | C11A—H11A | 0.9500 |
| C12—C13 | 1.358 (12) | C12A—C13A | 1.36 (2) |
| C12—H12 | 0.9500 | C12A—H12A | 0.9500 |
| C13—C14 | 1.411 (11) | C13A—C14A | 1.421 (19) |
| C13—H13 | 0.9500 | C13A—H13A | 0.9500 |
| C14—C15 | 1.511 (10) | C14A—C15A | 1.522 (18) |
| C15—O8 | 1.440 (9) | C15A—O8A | 1.441 (19) |
| C15—C16 | 1.521 (9) | C15A—C16A | 1.514 (19) |
| C15—C20 | 1.528 (10) | C15A—C20A | 1.53 (2) |
| C16—C17 | 1.540 (8) | C16A—C17A | 1.537 (17) |
| C16—H16 | 1.0000 | C16A—H16A | 1.0000 |
| C17—C18 | 1.531 (9) | C17A—C18A | 1.516 (18) |
| C17—H17A | 0.9900 | C17A—H17C | 0.9900 |

| | | | |
|---|---|---|---|
| C17—H17B | 0.9900 | C17A—H17D | 0.9900 |
| C18—H18 | 1.0000 | C18A—H18A | 1.0000 |
| O1—H1A | 0.8400 | O1A—H1AB | 0.8400 |
| O2—H2 | 0.8400 | O2A—H2AA | 0.8400 |
| C19—O3 | 1.287 (12) | C19A—O3A | 1.29 (2) |
| C19—N1 | 1.315 (17) | C19A—N1A | 1.29 (3) |
| N1—H1B | 0.8800 | N1A—H1AC | 0.8800 |
| N1—H1C | 0.8800 | N1A—H1AD | 0.8800 |
| O5—H5 | 0.8400 | N2A—H2AB | 0.8800 |
| N2—H2A | 0.8800 | N2A—H2AC | 0.8800 |
| N2—H2B | 0.8800 | O7A—H7A | 0.8400 |
| O7—H7 | 0.8400 | C20A—H20D | 0.9800 |
| C20—H20A | 0.9800 | C20A—H20E | 0.9800 |
| C20—H20B | 0.9800 | C20A—H20F | 0.9800 |
| C20—H20C | 0.9800 | O8A—H8A | 0.8400 |
| | | | |
| O1—C1—C2 | 112.2 (8) | H20B—C20—H20C | 109.5 |
| O1—C1—C18 | 108.0 (8) | C15—O8—H8 | 109.5 |
| C2—C1—C18 | 112.5 (8) | O1A—C1A—C2A | 121 (3) |
| O1—C1—H1 | 108.0 | O1A—C1A—C18A | 111 (2) |
| C2—C1—H1 | 108.0 | C2A—C1A—C18A | 114.6 (18) |
| C18—C1—H1 | 108.0 | O1A—C1A—H1AA | 102.7 |
| O2—C2—C3 | 124.4 (11) | C2A—C1A—H1AA | 102.7 |
| O2—C2—C1 | 115.0 (11) | C18A—C1A—H1AA | 102.7 |
| C3—C2—C1 | 120.6 (7) | O2A—C2A—C3A | 140 (3) |
| C19—C3—C2 | 120.5 (10) | O2A—C2A—C1A | 100 (3) |
| C19—C3—C4 | 117.9 (11) | C3A—C2A—C1A | 120.4 (16) |
| C2—C3—C4 | 121.5 (9) | C19A—C3A—C4A | 134 (3) |
| O4—C4—C3 | 125.9 (9) | C19A—C3A—C2A | 103 (2) |
| O4—C4—C5 | 118.4 (7) | C4A—C3A—C2A | 121.8 (19) |
| C3—C4—C5 | 115.6 (9) | O4A—C4A—C3A | 120 (2) |
| O5—C5—C18 | 111.9 (7) | O4A—C4A—C5A | 123 (2) |
| O5—C5—C6 | 109.6 (6) | C3A—C4A—C5A | 115.2 (18) |
| C18—C5—C6 | 109.0 (7) | C18A—C5A—C6A | 110.7 (18) |
| O5—C5—C4 | 102.9 (6) | C18A—C5A—C4A | 112.8 (19) |
| C18—C5—C4 | 112.2 (7) | C6A—C5A—C4A | 110 (2) |
| C6—C5—C4 | 111.1 (8) | N2A—C6A—C7A | 125 (4) |
| N2—C6—C7 | 123.0 (8) | N2A—C6A—C5A | 103 (3) |

| | | | |
|---|---|---|---|
| N2—C6—C5 | 116.9 (8) | C7A—C6A—C5A | 118 (2) |
| C7—C6—C5 | 118.6 (7) | C6A—C7A—C8A | 116.5 (19) |
| C6—C7—C8 | 121.4 (7) | C6A—C7A—C16A | 123.4 (18) |
| C6—C7—C16 | 122.1 (6) | C8A—C7A—C16A | 117.5 (16) |
| C8—C7—C16 | 115.8 (6) | O6A—C8A—C7A | 117 (2) |
| O6—C8—C7 | 122.5 (7) | O6A—C8A—C9A | 123 (2) |
| O6—C8—C9 | 119.1 (6) | C7A—C8A—C9A | 119.8 (17) |
| C7—C8—C9 | 118.4 (7) | C14A—C9A—C10A | 117.8 (19) |
| C14—C9—C10 | 116.6 (7) | C14A—C9A—C8A | 119.9 (17) |
| C14—C9—C8 | 121.2 (6) | C10A—C9A—C8A | 117 (2) |
| C10—C9—C8 | 121.9 (8) | C11A—C10A—O7A | 123 (2) |
| C11—C10—O7 | 118.0 (8) | C11A—C10A—C9A | 121 (2) |
| C11—C10—C9 | 122.7 (9) | O7A—C10A—C9A | 116 (2) |
| O7—C10—C9 | 119.3 (8) | C10A—C11A—C12A | 119 (2) |
| C10—C11—C12 | 119.1 (8) | C10A—C11A—H11A | 120.6 |
| C10—C11—H11 | 120.5 | C12A—C11A—H11A | 120.6 |
| C12—C11—H11 | 120.5 | C13A—C12A—C11A | 121 (2) |
| C13—C12—C11 | 120.2 (8) | C13A—C12A—H12A | 119.6 |
| C13—C12—H12 | 119.9 | C11A—C12A—H12A | 119.6 |
| C11—C12—H12 | 119.9 | C12A—C13A—C14A | 120 (2) |
| C12—C13—C14 | 121.0 (9) | C12A—C13A—H13A | 119.9 |
| C12—C13—H13 | 119.5 | C14A—C13A—H13A | 119.9 |
| C14—C13—H13 | 119.5 | C9A—C14A—C13A | 118.3 (18) |
| C9—C14—C13 | 119.9 (7) | C9A—C14A—C15A | 118.0 (18) |
| C9—C14—C15 | 118.7 (7) | C13A—C14A—C15A | 122 (2) |
| C13—C14—C15 | 121.4 (8) | O8A—C15A—C16A | 117 (3) |
| O8—C15—C14 | 107.5 (8) | O8A—C15A—C14A | 111 (3) |
| O8—C15—C16 | 106.9 (8) | C16A—C15A—C14A | 110.1 (18) |
| C14—C15—C16 | 109.1 (6) | O8A—C15A—C20A | 98 (4) |
| O8—C15—C20 | 111.3 (9) | C16A—C15A—C20A | 114 (4) |
| C14—C15—C20 | 109.8 (8) | C14A—C15A—C20A | 105 (3) |
| C16—C15—C20 | 112.2 (9) | C7A—C16A—C15A | 113 (2) |
| C7—C16—C15 | 112.7 (6) | C7A—C16A—C17A | 113.8 (16) |
| C7—C16—C17 | 113.2 (6) | C15A—C16A—C17A | 117 (2) |
| C15—C16—C17 | 109.7 (6) | C7A—C16A—H16A | 103.9 |
| C7—C16—H16 | 106.9 | C15A—C16A—H16A | 103.9 |
| C15—C16—H16 | 106.9 | C17A—C16A—H16A | 103.9 |
| C17—C16—H16 | 106.9 | C18A—C17A—C16A | 117.1 (19) |

| | | | |
|---|---|---|---|
| C18—C17—C16 | 113.3 (7) | C18A—C17A—H17C | 108.0 |
| C18—C17—H17A | 108.9 | C16A—C17A—H17C | 108.0 |
| C16—C17—H17A | 108.9 | C18A—C17A—H17D | 108.0 |
| C18—C17—H17B | 108.9 | C16A—C17A—H17D | 108.0 |
| C16—C17—H17B | 108.9 | H17C—C17A—H17D | 107.3 |
| H17A—C17—H17B | 107.7 | C5A—C18A—C17A | 113.1 (19) |
| C5—C18—C1 | 109.3 (7) | C5A—C18A—C1A | 109.8 (17) |
| C5—C18—C17 | 108.2 (7) | C17A—C18A—C1A | 114 (2) |
| C1—C18—C17 | 109.3 (7) | C5A—C18A—H18A | 106.5 |
| C5—C18—H18 | 110.0 | C17A—C18A—H18A | 106.5 |
| C1—C18—H18 | 110.0 | C1A—C18A—H18A | 106.5 |
| C17—C18—H18 | 110.0 | C1A—O1A—H1AB | 109.5 |
| C1—O1—H1A | 109.5 | C2A—O2A—H2AA | 109.5 |
| C2—O2—H2 | 109.5 | O3A—C19A—N1A | 122 (3) |
| O3—C19—N1 | 118.9 (11) | O3A—C19A—C3A | 127 (3) |
| O3—C19—C3 | 123.5 (14) | N1A—C19A—C3A | 110 (3) |
| N1—C19—C3 | 117.6 (10) | C19A—N1A—H1AC | 120.0 |
| C19—N1—H1B | 120.0 | C19A—N1A—H1AD | 120.0 |
| C19—N1—H1C | 120.0 | H1AC—N1A—H1AD | 120.0 |
| H1B—N1—H1C | 120.0 | C6A—N2A—H2AB | 120.0 |
| C5—O5—H5 | 109.5 | C6A—N2A—H2AC | 120.0 |
| C6—N2—H2A | 120.0 | H2AB—N2A—H2AC | 120.0 |
| C6—N2—H2B | 120.0 | C10A—O7A—H7A | 109.5 |
| H2A—N2—H2B | 120.0 | C15A—C20A—H20D | 109.5 |
| C10—O7—H7 | 109.5 | C15A—C20A—H20E | 109.5 |
| C15—C20—H20A | 109.5 | H20D—C20A—H20E | 109.5 |
| C15—C20—H20B | 109.5 | C15A—C20A—H20F | 109.5 |
| H20A—C20—H20B | 109.5 | H20D—C20A—H20F | 109.5 |
| C15—C20—H20C | 109.5 | H20E—C20A—H20F | 109.5 |
| H20A—C20—H20C | 109.5 | C15A—O8A—H8A | 109.5 |
| | | | |
| O1—C1—C2—O2 | -27.6 (12) | C4—C3—C19—O3 | -177.8 (9) |
| C18—C1—C2—O2 | -149.7 (8) | C2—C3—C19—N1 | 177.4 (9) |
| O1—C1—C2—C3 | 152.1 (8) | C4—C3—C19—N1 | 1.4 (14) |
| C18—C1—C2—C3 | 30.0 (12) | O1A—C1A—C2A—O2A | -30 (4) |
| O2—C2—C3—C19 | -3.8 (15) | C18A—C1A—C2A—O2A | -166 (3) |
| C1—C2—C3—C19 | 176.5 (9) | O1A—C1A—C2A—C3A | 151 (3) |
| O2—C2—C3—C4 | 172.0 (9) | C18A—C1A—C2A—C3A | 15 (4) |

| | | | |
|---|---|---|---|
| C1—C2—C3—C4 | -7.6 (13) | O2A—C2A—C3A—C19A | 6 (6) |
| C19—C3—C4—O4 | 5.4 (14) | C1A—C2A—C3A—C19A | -175 (3) |
| C2—C3—C4—O4 | -170.5 (8) | O2A—C2A—C3A—C4A | -168 (4) |
| C19—C3—C4—C5 | -173.8 (8) | C1A—C2A—C3A—C4A | 11 (5) |
| C2—C3—C4—C5 | 10.3 (12) | C19A—C3A—C4A—O4A | 23 (6) |
| O4—C4—C5—O5 | -95.1 (8) | C2A—C3A—C4A—O4A | -166 (3) |
| C3—C4—C5—O5 | 84.2 (8) | C19A—C3A—C4A—C5A | -173 (4) |
| O4—C4—C5—C18 | 144.4 (8) | C2A—C3A—C4A—C5A | -2 (4) |
| C3—C4—C5—C18 | -36.3 (10) | O4A—C4A—C5A—C18A | 130 (3) |
| O4—C4—C5—C6 | 22.1 (11) | C3A—C4A—C5A—C18A | -33 (3) |
| C3—C4—C5—C6 | -158.7 (7) | O4A—C4A—C5A—C6A | 6 (4) |
| O5—C5—C6—N2 | 17.1 (14) | C3A—C4A—C5A—C6A | -157 (3) |
| C18—C5—C6—N2 | 139.9 (13) | C18A—C5A—C6A—N2A | 174 (4) |
| C4—C5—C6—N2 | -95.9 (13) | C4A—C5A—C6A—N2A | -61 (4) |
| O5—C5—C6—C7 | -149.2 (10) | C18A—C5A—C6A—C7A | -44 (4) |
| C18—C5—C6—C7 | -26.3 (12) | C4A—C5A—C6A—C7A | 82 (4) |
| C4—C5—C6—C7 | 97.8 (11) | N2A—C6A—C7A—C8A | -41 (6) |
| N2—C6—C7—C8 | 7.4 (19) | C5A—C6A—C7A—C8A | -174 (3) |
| C5—C6—C7—C8 | 172.7 (8) | N2A—C6A—C7A—C16A | 158 (4) |
| N2—C6—C7—C16 | 176.9 (12) | C5A—C6A—C7A—C16A | 25 (6) |
| C5—C6—C7—C16 | -17.7 (15) | C6A—C7A—C8A—O6A | 29 (5) |
| C6—C7—C8—O6 | -2.0 (13) | C16A—C7A—C8A—O6A | -168 (3) |
| C16—C7—C8—O6 | -172.2 (8) | C6A—C7A—C8A—C9A | -147 (4) |
| C6—C7—C8—C9 | 175.3 (10) | C16A—C7A—C8A—C9A | 15 (5) |
| C16—C7—C8—C9 | 5.1 (11) | O6A—C8A—C9A—C14A | 177 (4) |
| O6—C8—C9—C14 | -166.6 (9) | C7A—C8A—C9A—C14A | -7 (6) |
| C7—C8—C9—C14 | 15.9 (14) | O6A—C8A—C9A—C10A | 23 (6) |
| O6—C8—C9—C10 | 8.1 (14) | C7A—C8A—C9A—C10A | -161 (3) |
| C7—C8—C9—C10 | -169.4 (8) | C14A—C9A—C10A—C11A | 15 (6) |
| C14—C9—C10—C11 | -7.8 (14) | C8A—C9A—C10A—C11A | 170 (3) |
| C8—C9—C10—C11 | 177.3 (9) | C14A—C9A—C10A—O7A | -170 (4) |
| C14—C9—C10—O7 | 174.5 (9) | C8A—C9A—C10A—O7A | -16 (5) |
| C8—C9—C10—O7 | -0.4 (14) | O7A—C10A—C11A—C12A | 175 (4) |
| O7—C10—C11—C12 | -178.5 (8) | C9A—C10A—C11A—C12A | -11 (6) |
| C9—C10—C11—C12 | 3.7 (13) | C10A—C11A—C12A—C13A | 9 (7) |
| C10—C11—C12—C13 | 0.7 (13) | C11A—C12A—C13A—C14A | -11 (7) |
| C11—C12—C13—C14 | -0.7 (14) | C10A—C9A—C14A—C13A | -17 (6) |
| C10—C9—C14—C13 | 7.5 (15) | C8A—C9A—C14A—C13A | -171 (3) |

| | | | |
|---|---|---|---|
| C8—C9—C14—C13 | -177.5 (9) | C10A—C9A—C14A—C15A | 176 (3) |
| C10—C9—C14—C15 | -173.6 (8) | C8A—C9A—C14A—C15A | 22 (6) |
| C8—C9—C14—C15 | 1.3 (15) | C12A—C13A—C14A—C9A | 15 (6) |
| C12—C13—C14—C9 | -3.6 (15) | C12A—C13A—C14A—C15A | -178 (4) |
| C12—C13—C14—C15 | 177.6 (9) | C9A—C14A—C15A—O8A | -176 (4) |
| C9—C14—C15—O8 | -152.2 (10) | C13A—C14A—C15A—O8A | 18 (5) |
| C13—C14—C15—O8 | 26.6 (12) | C9A—C14A—C15A—C16A | -45 (5) |
| C9—C14—C15—C16 | -36.7 (12) | C13A—C14A—C15A—C16A | 149 (4) |
| C13—C14—C15—C16 | 142.1 (9) | C9A—C14A—C15A—C20A | 79 (5) |
| C9—C14—C15—C20 | 86.7 (11) | C13A—C14A—C15A—C20A | -87 (5) |
| C13—C14—C15—C20 | -94.5 (12) | C6A—C7A—C16A—C15A | 122 (4) |
| C6—C7—C16—C15 | 148.2 (10) | C8A—C7A—C16A—C15A | -39 (4) |
| C8—C7—C16—C15 | -41.7 (10) | C6A—C7A—C16A—C17A | -14 (5) |
| C6—C7—C16—C17 | 22.9 (13) | C8A—C7A—C16A—C17A | -175 (3) |
| C8—C7—C16—C17 | -167.0 (7) | O8A—C15A—C16A—C7A | 179 (3) |
| O8—C15—C16—C7 | 172.2 (8) | C14A—C15A—C16A—C7A | 52 (4) |
| C14—C15—C16—C7 | 56.3 (10) | C20A—C15A—C16A—C7A | -66 (3) |
| C20—C15—C16—C7 | -65.6 (9) | O8A—C15A—C16A—C17A | -46 (4) |
| O8—C15—C16—C17 | -60.6 (10) | C14A—C15A—C16A—C17A | -174 (3) |
| C14—C15—C16—C17 | -176.5 (8) | C20A—C15A—C16A—C17A | 68 (4) |
| C20—C15—C16—C17 | 61.6 (10) | C7A—C16A—C17A—C18A | 23 (5) |
| C7—C16—C17—C18 | 15.8 (11) | C15A—C16A—C17A—C18A | -111 (3) |
| C15—C16—C17—C18 | -111.1 (9) | C6A—C5A—C18A—C17A | 53 (3) |
| O5—C5—C18—C1 | -57.0 (9) | C4A—C5A—C18A—C17A | -71 (3) |
| C6—C5—C18—C1 | -178.4 (8) | C6A—C5A—C18A—C1A | -179 (3) |
| C4—C5—C18—C1 | 58.0 (9) | C4A—C5A—C18A—C1A | 57 (3) |
| O5—C5—C18—C17 | -175.9 (6) | C16A—C17A—C18A—C5A | -45 (4) |
| C6—C5—C18—C17 | 62.6 (9) | C16A—C17A—C18A—C1A | -171 (3) |
| C4—C5—C18—C17 | -60.9 (9) | O1A—C1A—C18A—C5A | 171 (3) |
| O1—C1—C18—C5 | -179.2 (8) | C2A—C1A—C18A—C5A | -48 (3) |
| C2—C1—C18—C5 | -54.8 (10) | O1A—C1A—C18A—C17A | -61 (4) |
| O1—C1—C18—C17 | -61.0 (11) | C2A—C1A—C18A—C17A | 79 (3) |
| C2—C1—C18—C17 | 63.4 (11) | C4A—C3A—C19A—O3A | 164 (4) |
| C16—C17—C18—C5 | -58.2 (10) | C2A—C3A—C19A—O3A | -8 (6) |
| C16—C17—C18—C1 | -177.1 (8) | C4A—C3A—C19A—N1A | -7 (6) |
| C2—C3—C19—O3 | -1.8 (16) | C2A—C3A—C19A—N1A | -180 (3) |

## VIII. Hydrogen-bond parameters

| *D*—H···*A* | *D*—H (Å) | H···*A* (Å) | *D*···*A* (Å) | *D*—H···*A* (°) |
|---|---|---|---|---|
| O2—H2···O3 | 0.84 | 1.94 | 2.666 (14) | 144.5 |
| N1—H1C···O4 | 0.88 | 1.75 | 2.472 (12) | 137.2 |
| N1—H1C···O4A | 0.88 | 2.10 | 2.90 (3) | 152.2 |
| O5—H5···O3A$^{i}$ | 0.84 | 2.36 | 2.92 (3) | 124.7 |
| N2—H2A···O6 | 0.88 | 1.98 | 2.633 (12) | 130.3 |
| N2—H2A···O6A | 0.88 | 1.62 | 2.28 (3) | 129.8 |
| O8—H8···O5$^{ii}$ | 0.84 | 1.88 | 2.693 (10) | 162.8 |
| O8—H8···O5A$^{ii}$ | 0.84 | 1.88 | 2.693 (10) | 162.8 |

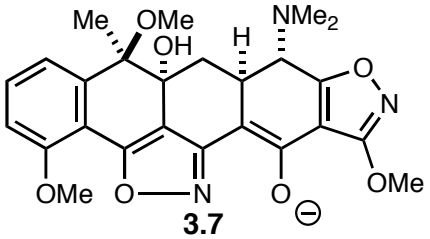
# *Appendix 4*

## Computed Geometries and Energies

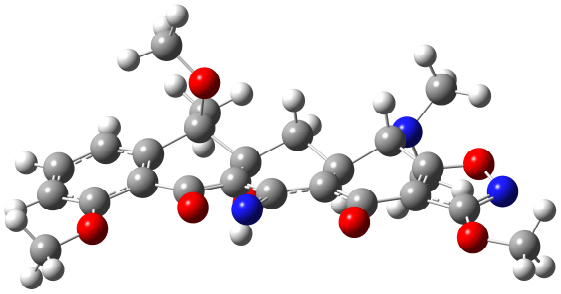
### I. Geometries and Energies Relevant to Chapter 3

DFT structures were verified to be true local minima by standard frequency analyses. Free energies are given at 298.15 K in all cases.

Equatorial dimethylamine **3.7**
Free energy: -1040779.92 kcal




**3.7**

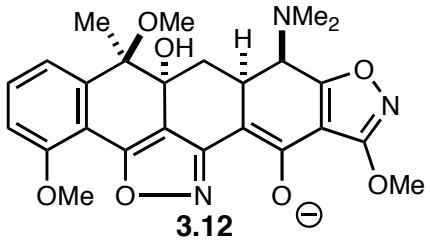


| | | | |
|---|---|---|---|
| H | 4.96399300 | -2.54305000 | -0.46163100 |
| C | 4.89327900 | -1.46279100 | -0.40463300 |
| C | 4.77635700 | 1.32251000 | -0.28196600 |
| C | 3.66266900 | -0.85475100 | -0.13742500 |
| C | 6.04635900 | -0.70327900 | -0.60093200 |
| C | 5.99779100 | 0.68754400 | -0.53154300 |

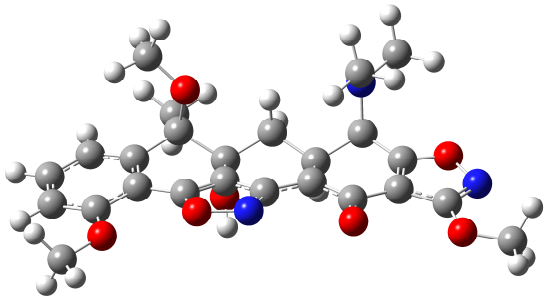
| | | | |
|---|---|---|---|
| C | 3.59992800 | 0.56538700 | -0.08402900 |
| H | 6.99353400 | -1.19704500 | -0.80504300 |
| H | 6.90126000 | 1.26752100 | -0.68279800 |
| C | 2.40669800 | -1.70313300 | 0.21123200 |
| O | 2.20840700 | -1.66812500 | 1.64297900 |
| C | 3.24850500 | -2.13056500 | 2.47451800 |
| H | 4.18030600 | -1.56414700 | 2.34039400 |
| H | 3.46911600 | -3.20030800 | 2.33078800 |
| H | 2.89594400 | -1.98829100 | 3.50075900 |
| C | 2.50155600 | -3.15548500 | -0.27350100 |
| H | 3.34756300 | -3.69202200 | 0.16707600 |
| H | 2.59267800 | -3.18638800 | -1.36106400 |
| H | 1.58927400 | -3.68631600 | 0.01223300 |
| C | 1.10789600 | -1.03385500 | -0.36996300 |
| C | -0.21940400 | -1.57538400 | 0.18252400 |
| C | -1.42109600 | -0.69920200 | -0.25796600 |
| C | -2.72135200 | -1.38751500 | 0.26052800 |
| H | -2.57961000 | -1.55407300 | 1.34031000 |
| N | -2.93568300 | -2.72319800 | -0.32370300 |
| C | -3.76056600 | -3.59957500 | 0.49594500 |
| H | -3.37776000 | -3.60948600 | 1.52288600 |
| H | -3.69631500 | -4.62376300 | 0.10387400 |
| H | -4.82699500 | -3.31461800 | 0.52954000 |
| C | -3.85476200 | -0.41015900 | 0.11196800 |
| C | -3.73227400 | 0.94168200 | 0.11643400 |
| C | -5.09537500 | 1.37083700 | 0.04231800 |
| O | -5.50302500 | 2.65138100 | 0.00797000 |
| C | -6.91074300 | 2.84621000 | -0.07199600 |
| H | -7.32201200 | 2.39770700 | -0.98438500 |
| H | -7.05883700 | 3.92833400 | -0.08293400 |
| H | -7.42129100 | 2.40235700 | 0.79102000 |
| N | -5.95773400 | 0.37024100 | -0.00632200 |
| O | -5.15351500 | -0.79513800 | 0.05047100 |
| C | -2.41707100 | 1.65194500 | 0.26490300 |
| C | 0.04337700 | 1.28327000 | 0.21071000 |
| N | 0.50294300 | 2.51738700 | 0.48581200 |
| O | 1.96318500 | 2.41197400 | 0.40232100 |
| C | 2.27484400 | 1.14613800 | 0.08962500 |
| C | 1.14897800 | 0.41008400 | -0.05653200 |
| C | -1.29587600 | 0.78166200 | 0.16647900 |
| O | 4.62931400 | 2.67807000 | -0.22638400 |
| C | 5.76400900 | 3.49268600 | -0.42691100 |
| H | 6.53641300 | 3.31486500 | 0.33556000 |
| H | 5.40812700 | 4.52159100 | -0.34383300 |
| H | 6.20715900 | 3.34193600 | -1.42218000 |
| O | 1.13637700 | -1.26035200 | -1.80841100 |

| | | | |
|---|---|---|---|
| H | 1.21877100 | -0.38184500 | -2.20986000 |
| O | -2.40735000 | 2.88205600 | 0.47613300 |
| H | -1.45501000 | -0.76366000 | -1.36107800 |
| H | -0.16192900 | -1.58665100 | 1.27639700 |
| H | -0.38883200 | -2.59876000 | -0.16525000 |
| C | -3.35930700 | -2.74251600 | -1.71860100 |
| H | -4.39733900 | -2.39822900 | -1.87131400 |
| H | -3.28182500 | -3.77012700 | -2.09698900 |
| H | -2.69675200 | -2.11592600 | -2.32073700 |

Axial dimethylamine **3.12**
Free energy: -1040779.72 kcal



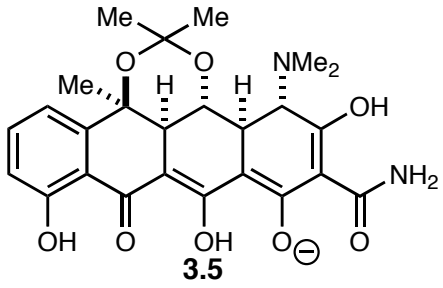

**3.12**



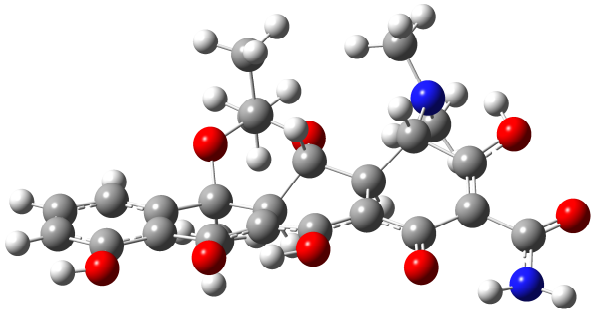
| | | | |
|---|---|---|---|
| H | 5.04231800 | -2.30828400 | -1.02911500 |
| C | 4.93167500 | -1.27005000 | -0.73778000 |
| C | 4.71352500 | 1.41414600 | -0.00748000 |
| C | 3.67231300 | -0.76982300 | -0.39287400 |
| C | 6.06322900 | -0.45510900 | -0.71572600 |
| C | 5.96395300 | 0.88363100 | -0.34271800 |
| C | 3.55824700 | 0.60111700 | -0.03102600 |
| H | 7.03316500 | -0.86554900 | -0.98654600 |
| H | 6.85094000 | 1.50683400 | -0.32618700 |
| C | 2.43677900 | -1.70887400 | -0.28716700 |
| O | 2.19470300 | -1.99497000 | 1.10894400 |
| C | 3.21988700 | -2.61136000 | 1.85463100 |
| H | 4.14163900 | -2.01382700 | 1.88111500 |
| H | 3.47024700 | -3.61937400 | 1.48763900 |
| H | 2.83250100 | -2.70439700 | 2.87385000 |
| C | 2.59855900 | -3.01534100 | -1.07515500 |
| H | 3.45510800 | -3.60690000 | -0.73776600 |
| H | 2.71479500 | -2.80249400 | -2.13980000 |
| H | 1.70219000 | -3.62652100 | -0.93824200 |
| C | 1.13212300 | -0.96637000 | -0.75281300 |
| C | -0.18986400 | -1.65751800 | -0.37961300 |
| C | -1.41007300 | -0.74003700 | -0.65122000 |

| | | | |
|---|---|---|---|
| C | -2.72184400 | -1.55288700 | -0.39460400 |
| C | -3.85244600 | -0.57137000 | -0.48243900 |
| C | -3.77486400 | 0.75522500 | -0.19667300 |
| C | -5.13633000 | 1.17573200 | -0.34046000 |
| O | -5.58090200 | 2.43265300 | -0.16798100 |
| C | -6.97781600 | 2.62244000 | -0.36490000 |
| H | -7.27348500 | 2.35905000 | -1.38759800 |
| H | -7.16057000 | 3.68329900 | -0.17990500 |
| H | -7.56243000 | 2.00975100 | 0.33172400 |
| N | -5.95398100 | 0.19444900 | -0.67903000 |
| O | -5.12433700 | -0.94969100 | -0.76605500 |
| N | 0.37994100 | 2.30975500 | 0.80153200 |
| O | 1.84311400 | 2.25969900 | 0.76286800 |
| C | 2.20903400 | 1.09311600 | 0.21181500 |
| C | 1.11474100 | 0.37374300 | -0.12801600 |
| O | 4.51799200 | 2.71811200 | 0.34420200 |
| C | 5.62992700 | 3.58634900 | 0.37867200 |
| H | 6.38347900 | 3.25867300 | 1.10966800 |
| H | 5.23647300 | 4.55918500 | 0.68033200 |
| H | 6.10906200 | 3.67951600 | -0.60690300 |
| O | 1.22366000 | -0.86866800 | -2.20330800 |
| H | 1.14503900 | 0.07523200 | -2.40889800 |
| H | -1.42843700 | -0.58684000 | -1.74803300 |
| H | -0.16078000 | -1.93990800 | 0.67409700 |
| H | -0.30367400 | -2.57803400 | -0.96595300 |
| C | -0.02737700 | 1.14778300 | 0.26139400 |
| N | -2.72854700 | -2.36415400 | 0.84207200 |
| H | -2.81071100 | -2.28227600 | -1.21023600 |
| C | -3.73501000 | -3.41444300 | 0.82757600 |
| H | -3.57709100 | -4.07275700 | 1.69206300 |
| H | -4.77566600 | -3.04240100 | 0.86991200 |
| H | -3.63129200 | -4.01886200 | -0.08178100 |
| C | -2.76386800 | -1.61027000 | 2.09305300 |
| H | -2.02248100 | -0.80970200 | 2.06102100 |
| H | -3.74832900 | -1.15367800 | 2.30445100 |
| H | -2.52323600 | -2.29184200 | 2.91974200 |
| C | -1.34646300 | 0.63741600 | 0.04465700 |
| C | -2.50374100 | 1.45400300 | 0.19847900 |
| O | -2.55503700 | 2.62839700 | 0.61778900 |

Muxfeldt case **3.12**
Free energy: -1054091.48 kcal




**3.5**



| | | | |
|---|---|---|---|
| H | 4.73656343 | 1.91962934 | 0.80149823 |
| C | 4.77894068 | 0.86656904 | 0.54679244 |
| C | 4.85391865 | -1.82585080 | -0.17331840 |
| C | 3.58670369 | 0.13442476 | 0.45942934 |
| C | 6.00147194 | 0.26290944 | 0.28307848 |
| C | 6.03535056 | -1.08391498 | -0.06035536 |
| C | 3.58854386 | -1.21924904 | 0.06489445 |
| H | 6.92566054 | 0.83242251 | 0.34868658 |
| H | 6.98754854 | -1.57834796 | -0.25608816 |
| C | 2.30217073 | 0.88175912 | 0.83956081 |
| O | 2.34066959 | 2.04423968 | -0.02974232 |
| C | 1.22442768 | 2.91662238 | -0.13119485 |
| C | 2.40408114 | 1.29658872 | 2.32480989 |
| H | 3.24994127 | 1.96814550 | 2.50011447 |
| H | 2.54157181 | 0.40172519 | 2.94219570 |
| H | 1.48167633 | 1.78701457 | 2.65105686 |
| C | 0.98220593 | 0.08583946 | 0.64463005 |
| C | -0.05341929 | 0.87748478 | -0.17677821 |
| C | -1.44321931 | 0.28222631 | 0.12305104 |
| C | -2.61276551 | 0.80531098 | -0.75086140 |
| H | -2.38559815 | 0.54710679 | -1.79547134 |
| C | -3.91976252 | 0.06871642 | -0.36382615 |
| C | -3.93440863 | -1.20921400 | 0.10382931 |
| C | -2.64172556 | -1.98698657 | 0.06985382 |
| C | -1.40264727 | -1.25029316 | -0.03565209 |
| H | -1.67713164 | 0.55566425 | 1.16612271 |
| H | 0.17528093 | 0.77500180 | -1.24679529 |
| O | 4.93954788 | -3.14574098 | -0.51597116 |
| H | 5.88310073 | -3.34563165 | -0.62925384 |
| O | -0.00234391 | 2.27051612 | 0.19320274 |
| H | 0.53304668 | -0.00865564 | 1.64650712 |
| C | 2.30170088 | -1.96177431 | -0.17112070 |
| C | 1.09147902 | -1.28187827 | 0.04267234 |
| C | -0.16978544 | -1.92045138 | -0.21165725 |

| | | | |
|---|---|---|---|
| O | -0.15101168 | -3.18758696 | -0.62454434 |
| H | 0.83464051 | -3.43155141 | -0.68196512 |
| O | 2.36008288 | -3.16269019 | -0.59739881 |
| O | -2.68499422 | -3.23790397 | 0.13097723 |
| C | 1.34001992 | 4.11144793 | 0.82509305 |
| H | 2.27048242 | 4.65426113 | 0.62912801 |
| H | 0.49623185 | 4.79403855 | 0.67634764 |
| H | 1.33656582 | 3.78260593 | 1.86557472 |
| C | 1.27147450 | 3.39792824 | -1.59146781 |
| H | 0.56386874 | 4.21474358 | -1.76259427 |
| H | 2.28073966 | 3.75631289 | -1.81636795 |
| H | 1.04564241 | 2.57614245 | -2.27639597 |
| C | -5.24376689 | -1.84036892 | 0.50471866 |
| O | -6.32647630 | -1.25217653 | 0.46201799 |
| N | -5.14773140 | -3.12087084 | 0.98119275 |
| H | -6.03198390 | -3.59984397 | 1.08109051 |
| H | -4.28621823 | -3.62011414 | 0.73701190 |
| O | -5.01279439 | 0.81161737 | -0.56898450 |
| H | -4.61540824 | 1.68491770 | -0.85046560 |
| N | -2.96442504 | 2.24591416 | -0.74887971 |
| C | -2.39762254 | 3.06705709 | -1.80709019 |
| H | -2.96900931 | 4.00241128 | -1.87855876 |
| H | -1.34520739 | 3.31811862 | -1.64121657 |
| H | -2.48865154 | 2.54357008 | -2.76492793 |
| C | -2.99458033 | 2.90627870 | 0.55851197 |
| H | -1.99417899 | 3.10232318 | 0.95991682 |
| H | -3.53359502 | 3.85733011 | 0.45787984 |
| H | -3.54782455 | 2.28119452 | 1.26620754 |

Chlorine

$Cl_2$

Free energy: -577540.81 kcal

| | | | |
|---|---|---|---|
| Cl | 0.00000000 | 0.00000000 | 1.02118500 |
| Cl | 0.00000000 | 0.00000000 | -1.02118500 |

*Intermediate Enolate Chlorination Energies*

Equatorial dimethylamine **3.7**
*trans addition*

**trans_EqMe2N**

| C-Cl Distance (Å) | Energy (kcal) | Rel. energy (kcal) |
|---|---|---|
| 3.5 | -1618592.40 | 34.83 |
| 3.4 | -1618593.46 | 33.77 |
| 3.3 | -1618594.63 | 32.60 |
| 3.2 | -1618595.96 | 31.27 |
| 3.1 | -1618597.47 | 29.76 |
| 3.0 | -1618599.11 | 28.13 |
| 2.9 | -1618600.89 | 26.35 |
| 2.8 | -1618602.78 | 24.46 |
| 2.7 | -1618604.77 | 22.46 |
| 2.6 | -1618606.85 | 20.38 |
| 2.5 | -1618608.96 | 18.27 |
| 2.4 | -1618611.07 | 16.16 |
| 2.3 | -1618613.13 | 14.10 |
| 2.2 | -1618615.06 | 12.18 |
| 2.1 | -1618616.71 | 10.52 |

*cis addition*

**Cis_EqMe2N**

| C-Cl Distance (Å) | Energy (kcal) | Rel. energy (kcal) |
|---|---|---|
| 3.5 | -1618591.78 | 35.46 |
| 3.4 | -1618592.69 | 34.54 |
| 3.3 | -1618593.80 | 33.43 |
| 3.2 | -1618595.01 | 32.22 |
| 3.1 | -1618596.35 | 30.88 |
| 3.0 | -1618597.84 | 29.39 |
| 2.9 | -1618599.42 | 27.82 |
| 2.8 | -1618601.07 | 26.16 |
| 2.7 | -1618602.77 | 24.47 |
| 2.6 | -1618604.47 | 22.76 |
| 2.5 | -1618606.13 | 21.10 |
| 2.4 | -1618607.70 | 19.53 |
| 2.3 | -1618609.11 | 18.12 |
| 2.2 | -1618610.50 | 16.74 |
| 2.1 | -1618611.86 | 15.37 |

Axial dimethylamine **3.7**
*trans addition*

**trans_AxMe2N**

| C-Cl Distance (Å) | Energy (kcal) | Rel. energy (kcal) |
|---|---|---|
| 3.5 | -1618586.06 | 26.37 |
| 3.4 | -1618586.91 | 25.52 |
| 3.3 | -1618587.89 | 24.54 |
| 3.2 | -1618589.04 | 23.39 |
| 3.1 | -1618590.40 | 22.03 |
| 3.0 | -1618591.98 | 20.45 |
| 2.9 | -1618593.66 | 18.77 |
| 2.8 | -1618595.54 | 16.89 |
| 2.7 | -1618597.54 | 14.89 |
| 2.6 | -1618599.64 | 12.79 |
| 2.5 | -1618601.83 | 10.60 |
| 2.4 | -1618604.05 | 8.38 |
| 2.3 | -1618606.24 | 6.19 |
| 2.2 | -1618608.35 | 4.08 |
| 2.1 | -1618610.26 | 2.17 |

*cis addition*

**cis_AxMe2N**

| C-Cl Distance (Å) | Energy (kcal) | Rel. energy (kcal) |
|---|---|---|
| 3.5 | -1618591.80 | 20.63 |
| 3.4 | -1618592.86 | 19.57 |
| 3.3 | -1618594.03 | 18.40 |
| 3.2 | -1618595.31 | 17.12 |
| 3.1 | -1618596.70 | 15.73 |
| 3.0 | -1618598.21 | 14.22 |
| 2.9 | -1618599.81 | 12.62 |
| 2.8 | -1618601.49 | 10.94 |
| 2.7 | -1618603.23 | 9.20 |
| 2.6 | -1618604.98 | 7.45 |
| 2.5 | -1618606.69 | 5.74 |
| 2.4 | -1618608.28 | 4.15 |
| 2.3 | -1618609.69 | 2.74 |
| 2.2 | -1618610.85 | 1.58 |
| 2.1 | -1618611.68 | 0.75 |

Muxfeldt case **3.12**
*trans addition*

**cis_Muxfeldt**

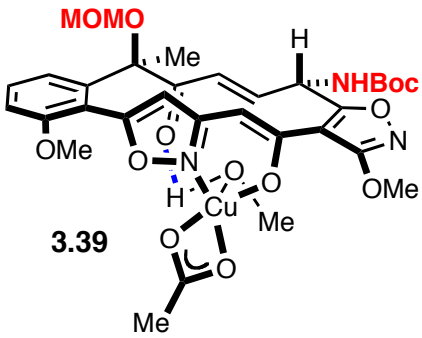
| C-Cl Distance (Å) | Energy (kcal) | Rel. energy (kcal) |
|---|---|---|
| 3.5 | -1631908.38 | 21.62 |
| 3.4 | -1631909.16 | 20.84 |
| 3.3 | -1631910.07 | 19.93 |
| 3.2 | -1631911.12 | 18.88 |
| 3.1 | -1631912.79 | 17.21 |
| 3.0 | -1631914.13 | 15.87 |
| 2.9 | -1631915.59 | 14.41 |
| 2.8 | -1631917.08 | 12.92 |
| 2.7 | -1631918.63 | 11.37 |
| 2.6 | -1631920.23 | 9.77 |
| 2.5 | -1631921.85 | 8.15 |
| 2.4 | -1631923.44 | 6.56 |
| 2.3 | -1631924.94 | 5.06 |
| 2.2 | -1631926.38 | 3.62 |
| 2.1 | -1631927.67 | 2.33 |

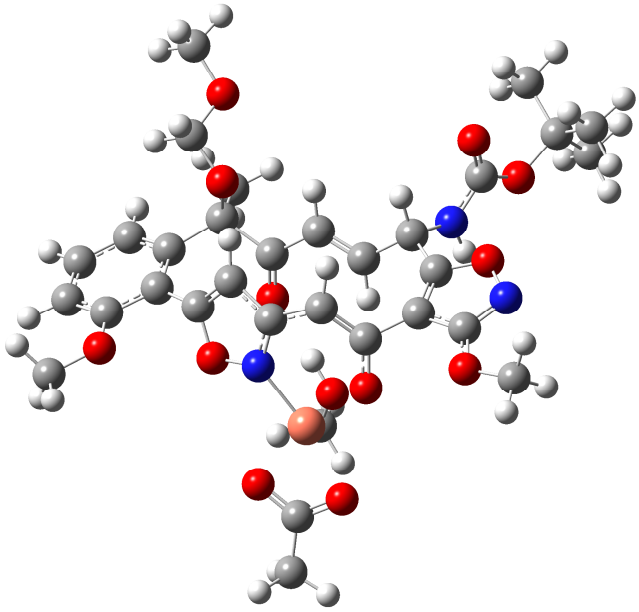
*cis addition*

**trans_Muxfeldt**

| C-Cl Distance (Å) | Energy (kcal) | Rel. energy (kcal) |
|---|---|---|
| 3.5 | -1631907.00 | 23.00 |
| 3.4 | -1631907.79 | 22.21 |
| 3.3 | -1631908.72 | 21.28 |
| 3.2 | -1631909.76 | 20.24 |
| 3.1 | -1631910.91 | 19.09 |
| 3.0 | -1631912.18 | 17.82 |
| 2.9 | -1631913.55 | 16.45 |
| 2.8 | -1631915.00 | 15.00 |
| 2.7 | -1631916.53 | 13.47 |
| 2.6 | -1631918.10 | 11.90 |
| 2.5 | -1631919.67 | 10.33 |
| 2.4 | -1631921.22 | 8.78 |
| 2.3 | -1631922.69 | 7.31 |
| 2.2 | -1631924.01 | 5.99 |
| 2.1 | -1631925.09 | 4.91 |

*Geometries and Energies for Macrocyclic Copper(II) Enolates*



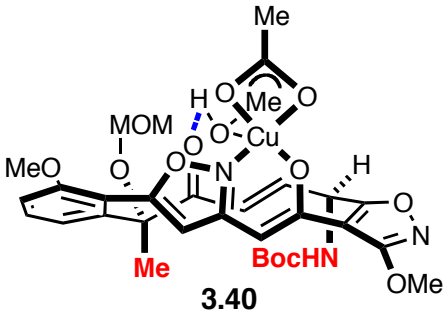



Enolate **3.39**
Free energy: -1620070.025 kcal

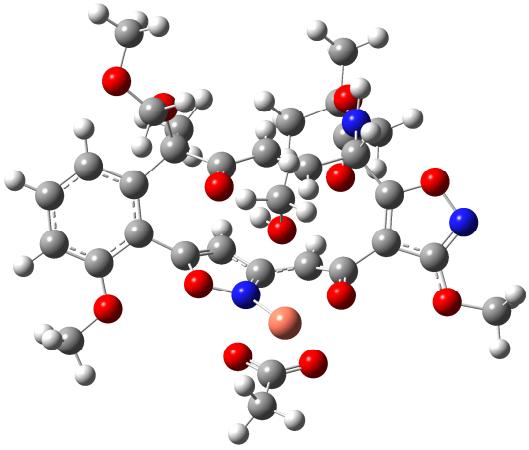
| | | | |
|---|---|---|---|
| H | 3.43746500 | 4.61752800 | 1.53126900 |
| C | 3.88682900 | 3.79507800 | 0.98949400 |
| C | 5.13805300 | 1.69864800 | -0.36088800 |
| C | 3.08307500 | 2.83074500 | 0.36846500 |
| C | 5.27904800 | 3.71697900 | 0.93349800 |
| C | 5.91729500 | 2.68176200 | 0.25751100 |
| C | 3.72759500 | 1.76655900 | -0.31229200 |
| H | 5.87696700 | 4.48010000 | 1.42411000 |
| H | 6.99928000 | 2.64151500 | 0.22084800 |
| C | 1.54836000 | 3.00727000 | 0.35319100 |
| O | 1.14673800 | 3.38888700 | -0.98571600 |
| C | 1.38329100 | 4.70174900 | -1.41514300 |
| H | 1.52295600 | 4.64747500 | -2.50386100 |
| H | 2.28773800 | 5.12995500 | -0.95898400 |
| C | 1.03065300 | 4.00257300 | 1.41326900 |
| H | -0.06192200 | 4.04486900 | 1.37831600 |
| H | 1.33583400 | 3.67264700 | 2.41051500 |
| H | 1.40732300 | 5.01342900 | 1.24605800 |
| C | 0.76465100 | 1.70482600 | 0.68497400 |
| C | -0.54898600 | 1.51039100 | 0.02942700 |
| C | -1.30985300 | 0.42212300 | 0.23715100 |
| C | -2.67653900 | 0.23336000 | -0.39584800 |
| H | -2.82415500 | 0.98379000 | -1.17886500 |

| | | | |
|---|---|---|---|
| C | -2.88514500 | -1.14477600 | -1.00712700 |
| C | -2.06270100 | -2.14683100 | -1.44031800 |
| C | -2.97924900 | -3.17713500 | -1.83026300 |
| O | -2.58928700 | -4.36088000 | -2.30838900 |
| C | -3.63562500 | -5.27331600 | -2.70029700 |
| H | -4.27133100 | -5.51747800 | -1.84367800 |
| H | -3.12301400 | -6.16735900 | -3.05603700 |
| N | -4.23860900 | -2.82367100 | -1.68688600 |
| O | -4.17801700 | -1.51918900 | -1.15063900 |
| C | -0.58137000 | -2.18295000 | -1.38701600 |
| C | 1.40060500 | -0.74850600 | -1.62410500 |
| N | 2.17661500 | -1.43677800 | -0.78379900 |
| O | 3.15434300 | -0.56192900 | -0.29380500 |
| C | 2.95873000 | 0.65187300 | -0.88485900 |
| C | 1.93242700 | 0.57128500 | -1.77370400 |
| O | 5.64933300 | 0.64026100 | -1.04663400 |
| C | 7.07092300 | 0.51295500 | -1.15436500 |
| H | 7.23825500 | -0.39159700 | -1.74153800 |
| H | 7.53408100 | 0.39958400 | -0.16775600 |
| O | 1.21379000 | 0.95508500 | 1.55571500 |
| H | -0.99671600 | -0.34607800 | 0.94080800 |
| H | -0.86451900 | 2.27493500 | -0.67105600 |
| C | -4.84453800 | 1.17389000 | 0.32759700 |
| O | -5.05903400 | 1.73515700 | -0.74437100 |
| O | -5.66193800 | 1.14644700 | 1.39577700 |
| C | -6.99376100 | 1.80084600 | 1.39078100 |
| C | -7.51464400 | 1.48031100 | 2.79273600 |
| H | -7.57936300 | 0.39748700 | 2.94644200 |
| H | -6.85439900 | 1.90073100 | 3.55940400 |
| H | -8.51387300 | 1.90761600 | 2.92667300 |
| C | -7.88220600 | 1.16111500 | 0.32220600 |
| H | -8.90230600 | 1.54979300 | 0.41799900 |
| H | -7.52596600 | 1.37960100 | -0.68672000 |
| H | -7.91872700 | 0.07391700 | 0.45491800 |
| C | -6.83091600 | 3.31036900 | 1.20443400 |
| H | -6.13850900 | 3.71671400 | 1.95050200 |
| H | -6.45839500 | 3.55824300 | 0.20825900 |
| H | -7.80170700 | 3.80032800 | 1.34010400 |
| N | -3.69264000 | 0.49841000 | 0.61823100 |
| H | -3.67480600 | -0.05371300 | 1.46863100 |
| C | 0.10808900 | -1.18335900 | -2.04294600 |
| H | -0.44068100 | -0.51450200 | -2.69386200 |
| O | 0.24782600 | 5.48866500 | -1.10856900 |
| C | 0.41968300 | 6.84681700 | -1.49814900 |
| H | 1.26228300 | 7.31503500 | -0.96800200 |
| H | -0.50238400 | 7.37215900 | -1.23691700 |

| | | | |
|---|---|---|---|
| O | -0.07632100 | -3.10407900 | -0.61606100 |
| H | 1.52692300 | 1.36513200 | -2.37929200 |
| H | 0.59072400 | 6.93808100 | -2.58097700 |
| H | 7.50689000 | 1.37289300 | -1.67520500 |
| H | -4.24016200 | -4.83781000 | -3.50164100 |
| Cu | 1.69421400 | -3.06720000 | 0.21152400 |
| O | 0.81865900 | -1.78788300 | 2.24134600 |
| H | 0.93031400 | -0.85021200 | 1.97943000 |
| C | 1.44309600 | -1.96288700 | 3.51466100 |
| H | 2.51851300 | -1.74508400 | 3.47568700 |
| H | 1.30548400 | -3.00772600 | 3.80660700 |
| H | 0.97875900 | -1.32281600 | 4.27730700 |
| O | 3.41290600 | -3.59983800 | 1.17041800 |
| C | 2.83864400 | -4.66910300 | 1.57789800 |
| O | 1.63219700 | -4.87009900 | 1.21681300 |
| C | 3.57618500 | -5.64263500 | 2.44844400 |
| H | 3.88049200 | -5.14303900 | 3.37511800 |
| H | 4.48788600 | -5.96905100 | 1.93575700 |
| H | 2.95523100 | -6.50899900 | 2.68505600 |




**3.40**

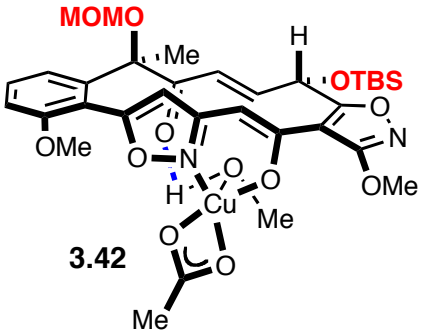


Enolate **3.40**
Free energy: -1620068.671 kcal

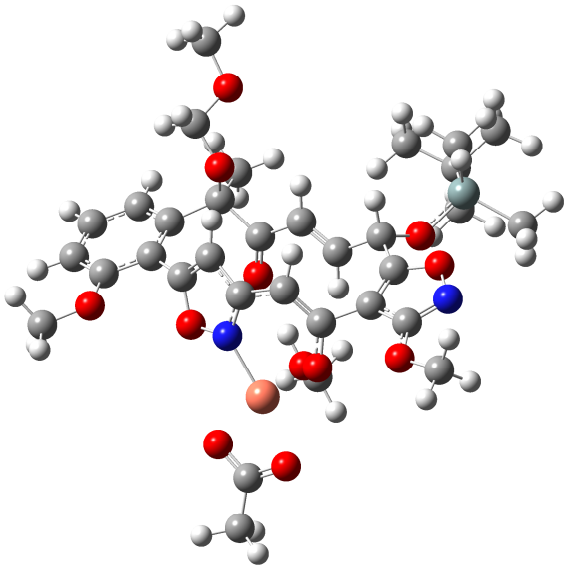
| | | | |
|---|---|---|---|
| H | 4.02847600 | -4.08154800 | 0.43542500 |
| C | 4.08345400 | -3.26573300 | -0.27537600 |
| C | 4.27754200 | -1.15911500 | -2.09109500 |
| C | 2.99935200 | -2.38203900 | -0.39213200 |
| C | 5.23531700 | -3.09262300 | -1.03738300 |
| C | 5.34843600 | -2.04304200 | -1.94845900 |

| | | | |
|---|---|---|---|
| C | 3.09905100 | -1.32459800 | -1.32315200 |
| H | 6.06349400 | -3.78663800 | -0.92174700 |
| H | 6.25224400 | -1.92406400 | -2.53376600 |
| C | 1.74198000 | -2.71104500 | 0.45434300 |
| O | 2.09707200 | -3.39176900 | 1.67907700 |
| C | 2.97326200 | -2.75682100 | 2.62045600 |
| H | 2.36642200 | -2.30925200 | 3.41949400 |
| H | 3.58613300 | -1.99469200 | 2.13820400 |
| C | 0.90496000 | -3.75613000 | -0.29671400 |
| H | 1.55444400 | -4.58161100 | -0.60193300 |
| H | 0.44344700 | -3.33477100 | -1.19304500 |
| H | 0.12388400 | -4.16389200 | 0.35137700 |
| C | 0.93706500 | -1.46385700 | 0.95337800 |
| C | -0.53948500 | -1.51594500 | 0.99468500 |
| C | -1.27318200 | -0.45532600 | 1.37866500 |
| C | -2.78089000 | -0.43057100 | 1.53364000 |
| H | -2.94584800 | -0.33209300 | 2.61729500 |
| C | -3.43826000 | 0.81012600 | 0.95213000 |
| C | -3.02754700 | 1.86772900 | 0.18968100 |
| C | -4.15915400 | 2.74678700 | 0.21579100 |
| O | -4.18241400 | 3.92272200 | -0.41436700 |
| C | -5.40863100 | 4.67790700 | -0.33081500 |
| H | -5.63400500 | 4.92569500 | 0.71097300 |
| H | -6.23640200 | 4.11003100 | -0.76637200 |
| N | -5.17347200 | 2.25883600 | 0.89717600 |
| O | -4.70479500 | 1.01908900 | 1.38381400 |
| C | -1.70056200 | 2.07121700 | -0.44066100 |
| C | 0.12805600 | 0.82149600 | -1.49489900 |
| N | 1.09696700 | 1.65441400 | -1.11501400 |
| O | 2.29870300 | 0.93650200 | -1.09197700 |
| C | 2.02136500 | -0.33820400 | -1.49093400 |
| C | 0.70802600 | -0.44371100 | -1.82496900 |
| O | 4.26229900 | -0.10882800 | -2.95728800 |
| C | 5.44125700 | 0.16999000 | -3.71899500 |
| H | 5.20270700 | 1.05293200 | -4.31464500 |
| H | 5.69039800 | -0.66316200 | -4.38595100 |
| O | 1.58587200 | -0.51933500 | 1.41748900 |
| H | -0.77704400 | 0.45439100 | 1.70841500 |
| H | -1.02841400 | -2.42732900 | 0.67379100 |
| C | -3.71463900 | -2.06643700 | -0.10604100 |
| O | -3.43573200 | -1.40700800 | -1.10485600 |
| O | -4.30377700 | -3.27633700 | -0.08940900 |
| C | -4.69574100 | -3.98320500 | -1.33464600 |
| C | -3.45462300 | -4.27202500 | -2.18162700 |
| H | -3.72858200 | -4.92605800 | -3.01701400 |
| H | -3.02000900 | -3.35730600 | -2.59042500 |

| | | | |
|---|---|---|---|
| H | -2.69417600 | -4.78717300 | -1.58341600 |
| C | -5.75230100 | -3.16976300 | -2.08405100 |
| H | -6.12517900 | -3.75577800 | -2.93151000 |
| H | -6.60019700 | -2.94556100 | -1.42687600 |
| H | -5.34641600 | -2.23087100 | -2.46705400 |
| C | -5.29590000 | -5.28162100 | -0.79350700 |
| H | -6.15563400 | -5.07373900 | -0.14704100 |
| H | -5.63370200 | -5.90908000 | -1.62479700 |
| H | -4.55366200 | -5.84426600 | -0.21653500 |
| N | -3.47751500 | -1.65637000 | 1.17225400 |
| H | -3.71961400 | -2.29383200 | 1.92013700 |
| C | -1.25799200 | 1.08894000 | -1.30261900 |
| H | -1.94756200 | 0.30915600 | -1.59492200 |
| O | 3.84616600 | -3.71415700 | 3.14202800 |
| C | 3.22465000 | -4.64749400 | 4.02913900 |
| H | 4.02327200 | -5.27357400 | 4.43484000 |
| H | 2.50067400 | -5.28239300 | 3.50478800 |
| O | -1.02870400 | 3.10745700 | -0.01967300 |
| H | 0.18283400 | -1.31663100 | -2.17969000 |
| H | 2.71789600 | -4.12641700 | 4.85334500 |
| H | 6.29103400 | 0.38893700 | -3.06274100 |
| H | -5.22924200 | 5.58675400 | -0.90569400 |
| Cu | 0.87822400 | 3.40917100 | -0.27763100 |
| O | 1.04142200 | 2.04161700 | 2.49273600 |
| C | 1.37080900 | 1.87994500 | 3.87258500 |
| H | 0.80824600 | 1.05473900 | 4.33097300 |
| H | 1.10425500 | 2.80819200 | 4.38649400 |
| H | 2.44461100 | 1.69611000 | 4.01842400 |
| O | 2.77044600 | 4.15208200 | -0.25734800 |
| C | 2.31384700 | 5.26580500 | 0.17922800 |
| O | 1.05427700 | 5.36218800 | 0.35431200 |
| C | 3.24183300 | 6.40340700 | 0.48227300 |
| H | 3.88036100 | 6.60040600 | -0.38534200 |
| H | 3.89544500 | 6.12008600 | 1.31588700 |
| H | 2.68523900 | 7.30438000 | 0.74783700 |
| H | 1.22500600 | 1.18775300 | 2.04938100 |




**3.42**

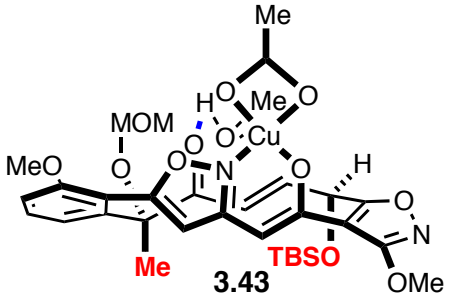


Enolate **3.42**
Free energy: -1745963.143 kcal

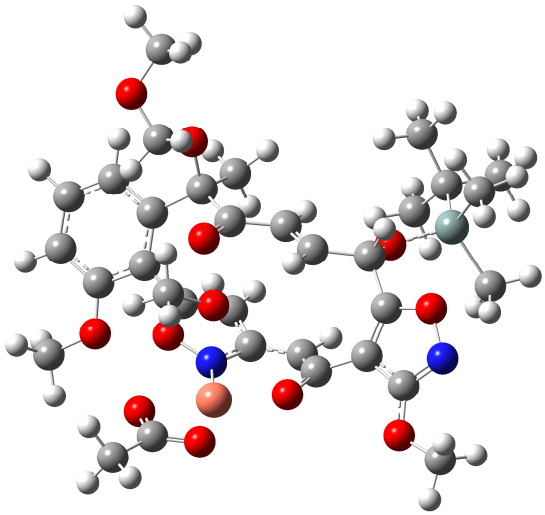
| | | | |
|---|---|---|---|
| H | -3.26127300 | -4.71514800 | 1.26144600 |
| C | -3.74459300 | -3.85840900 | 0.80973700 |
| C | -5.07928500 | -1.67507300 | -0.30195300 |
| C | -2.98095100 | -2.83666900 | 0.23186300 |
| C | -5.13843200 | -3.79403200 | 0.82810400 |
| C | -5.81804100 | -2.71504700 | 0.27173100 |
| C | -3.66725500 | -1.72890000 | -0.32839700 |
| H | -5.70449900 | -4.60202300 | 1.28327800 |
| H | -6.90086400 | -2.68610500 | 0.29001400 |
| C | -1.44544500 | -2.98928600 | 0.13948000 |
| O | -1.08524300 | -3.25789500 | -1.23704500 |
| C | -1.36835300 | -4.51825900 | -1.78035800 |
| H | -1.56779900 | -4.35503800 | -2.84883100 |
| H | -2.25214500 | -4.97898500 | -1.31615100 |
| C | -0.87446000 | -4.06274800 | 1.08989600 |
| H | 0.21544800 | -4.09019900 | 1.00056100 |
| H | -1.25124600 | -5.05933100 | 0.85113900 |
| H | -1.13469000 | -3.82273300 | 2.12473600 |
| C | -0.67172000 | -1.70206200 | 0.54618200 |
| C | 0.61408900 | -1.42093800 | -0.13326400 |
| C | 1.34556300 | -0.32069000 | 0.12114100 |
| C | 2.70059700 | -0.06319600 | -0.50777200 |
| H | 2.87217100 | -0.79247300 | -1.30974200 |
| C | 2.85841400 | 1.33034200 | -1.09789700 |

| | | | |
|---|---|---|---|
| C | 2.01240500 | 2.33661100 | -1.47343700 |
| C | 2.90351900 | 3.38373800 | -1.87729800 |
| O | 2.48484900 | 4.57421700 | -2.31202600 |
| C | 3.50714100 | 5.50362100 | -2.72677300 |
| H | 4.17602900 | 5.73423100 | -1.89200100 |
| H | 2.97373700 | 6.40081300 | -3.04184300 |
| N | 4.17004200 | 3.03748000 | -1.79601000 |
| O | 4.14052000 | 1.71984200 | -1.28969500 |
| C | 0.53388600 | 2.35079600 | -1.38413500 |
| C | -1.42080400 | 0.88064300 | -1.58922800 |
| N | -2.16365100 | 1.51439100 | -0.67952600 |
| O | -3.11660500 | 0.60925200 | -0.19838600 |
| C | -2.93495500 | -0.57092400 | -0.85996100 |
| C | -1.94690400 | -0.43400300 | -1.78418800 |
| O | -5.63441400 | -0.57282000 | -0.87517800 |
| C | -7.06033600 | -0.44634100 | -0.88719400 |
| H | -7.26402500 | 0.50184400 | -1.38777600 |
| H | -7.46278300 | -0.41578800 | 0.13156600 |
| O | -1.10380200 | -1.03927900 | 1.49259200 |
| H | 1.02778600 | 0.39692600 | 0.87472500 |
| H | 0.93581200 | -2.13107300 | -0.88664500 |
| C | -0.15343700 | 1.35084400 | -2.04049100 |
| H | 0.38667200 | 0.70762600 | -2.72347600 |
| O | -0.23123800 | -5.34547500 | -1.62270400 |
| C | -0.42096200 | -6.62158900 | -2.22483600 |
| H | -0.62731500 | -6.53127300 | -3.30173000 |
| H | 0.50756200 | -7.18100100 | -2.08550900 |
| O | 0.02556200 | 3.25303100 | -0.59282100 |
| C | -0.48588000 | 1.37073100 | 3.88589800 |
| H | 0.35479400 | 0.69885200 | 4.10789300 |
| H | -1.39840500 | 0.95343800 | 4.33438700 |
| H | -0.28649200 | 2.34290100 | 4.34604000 |
| O | -0.63451400 | 1.58247400 | 2.48132100 |
| H | -0.79268400 | 0.70792300 | 2.06946800 |
| H | -1.56119400 | -1.19082800 | -2.44677300 |
| H | -1.24773400 | -7.17287800 | -1.75320500 |
| H | -7.52582000 | -1.26398900 | -1.44897200 |
| H | 4.08088400 | 5.09043400 | -3.56189500 |
| C | -2.87301100 | 4.78792500 | 1.61170000 |
| C | -3.56019500 | 5.74563400 | 2.53726500 |
| H | -4.64576100 | 5.66395400 | 2.43910500 |
| H | -3.23603200 | 6.77063500 | 2.34092700 |
| H | -3.28975100 | 5.48917500 | 3.56957800 |
| O | -3.40939600 | 3.66858400 | 1.30257500 |
| O | -1.71883100 | 5.04263500 | 1.12821500 |
| Cu | -1.74828500 | 3.21337600 | 0.21191100 |

| | | | |
|---|---|---|---|
| O | 3.65965600 | -0.22007600 | 0.53424200 |
| Si | 5.14709900 | -1.05635100 | 0.50553200 |
| C | 4.99792300 | -2.48408600 | 1.77250800 |
| C | 5.50448800 | -1.68683300 | -1.23478400 |
| H | 4.75197000 | -2.39371900 | -1.60428000 |
| H | 5.56483700 | -0.85771100 | -1.95110400 |
| H | 6.47307600 | -2.20326300 | -1.25301400 |
| C | 6.45094200 | 0.19855500 | 1.02817400 |
| H | 6.20788300 | 0.66209300 | 1.99199900 |
| H | 7.44150400 | -0.26418800 | 1.12335300 |
| H | 6.53095700 | 1.00202600 | 0.28572600 |
| C | 4.66135700 | -1.91654000 | 3.16772100 |
| H | 5.44151800 | -1.23870500 | 3.53620400 |
| H | 3.71289600 | -1.36498500 | 3.16947500 |
| H | 4.56748500 | -2.73279300 | 3.89980800 |
| C | 3.88093100 | -3.45852100 | 1.34505400 |
| H | 4.08644100 | -3.92215600 | 0.37176100 |
| H | 3.77964900 | -4.27319600 | 2.07790900 |
| H | 2.90755700 | -2.95753900 | 1.27708100 |
| C | 6.33417900 | -3.25427500 | 1.85079500 |
| H | 7.16707200 | -2.61166800 | 2.16316500 |
| H | 6.26148100 | -4.06866400 | 2.58710900 |
| H | 6.60657400 | -3.70954200 | 0.88995500 |




**3.43**

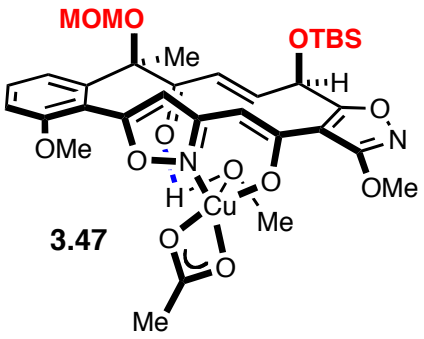


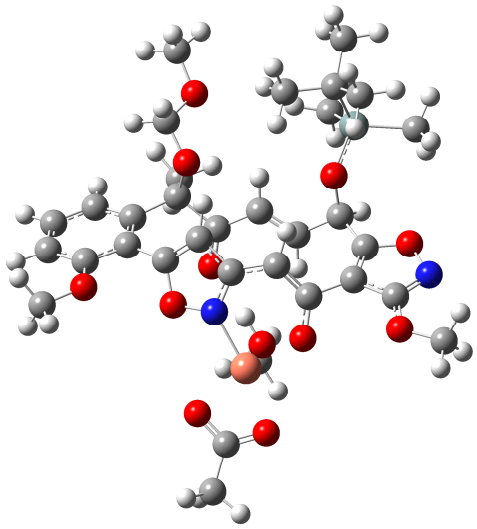
Enolate **3.43**
Free energy: -1745961.729 kcal

| | | | |
|---|---|---|---|
| H | 3.55204200 | -4.61474500 | 0.42932200 |
| C | 3.77716700 | -3.79718800 | -0.24551600 |
| C | 4.40524900 | -1.69782900 | -1.96963800 |
| C | 2.83600700 | -2.77078200 | -0.41975100 |

| | | | |
|---|---|---|---|
| C | 5.00036600 | -3.76864200 | -0.90930000 |
| C | 5.32946700 | -2.72536200 | -1.77433700 |
| C | 3.15454800 | -1.71772700 | -1.30528200 |
| H | 5.71390100 | -4.57286300 | -0.75174700 |
| H | 6.28544700 | -2.71995300 | -2.28398500 |
| C | 1.47544300 | -2.94510900 | 0.30235500 |
| O | 1.62149000 | -3.70126400 | 1.52373100 |
| C | 2.47599500 | -3.22540000 | 2.57156100 |
| H | 1.87075300 | -2.67193700 | 3.30255000 |
| H | 3.27013800 | -2.58945300 | 2.17815900 |
| C | 0.58459600 | -3.85109300 | -0.56022100 |
| H | 1.13967800 | -4.75889500 | -0.81358000 |
| H | 0.29239600 | -3.35913600 | -1.49141500 |
| H | -0.31408100 | -4.14508700 | -0.01032100 |
| C | 0.79499200 | -1.61259200 | 0.76936300 |
| C | -0.65903500 | -1.43748500 | 0.58736500 |
| C | -1.32272100 | -0.36737100 | 1.06207100 |
| C | -2.80625800 | -0.13467700 | 0.88850000 |
| H | -3.26174900 | -0.32678500 | 1.87430000 |
| C | -3.13605100 | 1.31464300 | 0.57732100 |
| C | -2.51804200 | 2.33719400 | -0.08774500 |
| C | -3.42849200 | 3.43279600 | 0.07665600 |
| O | -3.20649800 | 4.65198700 | -0.41577500 |
| C | -4.24003200 | 5.63468500 | -0.19599800 |
| H | -4.38908800 | 5.79901200 | 0.87550300 |
| H | -5.17795600 | 5.31106800 | -0.65744700 |
| N | -4.51476000 | 3.10025200 | 0.74206900 |
| O | -4.32043100 | 1.74354500 | 1.07553400 |
| C | -1.15318000 | 2.33450700 | -0.65878000 |
| C | 0.53631400 | 0.83589500 | -1.61645600 |
| N | 1.58698400 | 1.51050200 | -1.14589600 |
| O | 2.66585800 | 0.62398500 | -1.06201200 |
| C | 2.24017800 | -0.58680000 | -1.52022200 |
| C | 0.95237600 | -0.49275300 | -1.94720900 |
| O | 4.60676800 | -0.63416800 | -2.79501700 |
| C | 5.87223500 | -0.50278100 | -3.44984900 |
| H | 5.81106500 | 0.42737800 | -4.01760000 |
| H | 6.05359700 | -1.33791600 | -4.13578700 |
| O | 1.50047000 | -0.79692500 | 1.37474400 |
| H | -0.81045900 | 0.37456300 | 1.67058400 |
| H | -1.19101300 | -2.17226400 | -0.00116100 |
| C | -0.80724000 | 1.30143400 | -1.50747100 |
| H | -1.58433000 | 0.63916500 | -1.86674500 |
| O | 3.09334300 | -4.32476800 | 3.17304200 |
| C | 2.20686400 | -5.13403300 | 3.95019600 |
| H | 2.82126100 | -5.89989200 | 4.43019700 |

| | | | |
|---|---|---|---|
| H | 1.45053400 | -5.62006200 | 3.32292300 |
| O | -0.36033600 | 3.25644600 | -0.18898800 |
| H | 0.33651900 | -1.27438300 | -2.36359000 |
| H | 1.70535400 | -4.53466700 | 4.72281300 |
| H | 6.68828600 | -0.43486400 | -2.72159300 |
| H | -3.87931600 | 6.54665900 | -0.67199300 |
| Cu | 1.57972600 | 3.22629400 | -0.20367800 |
| O | 1.36460900 | 1.87113700 | 2.37072800 |
| C | 2.51603000 | 1.91963000 | 3.21439100 |
| H | 2.49065900 | 1.13070700 | 3.97913100 |
| H | 2.51332200 | 2.89047800 | 3.71854100 |
| H | 3.44886800 | 1.82613200 | 2.64152400 |
| O | 3.54714700 | 3.58366600 | 0.11180700 |
| C | 3.24761200 | 4.70206100 | 0.66106500 |
| O | 2.01496500 | 5.02102900 | 0.71654400 |
| C | 4.32122000 | 5.58826800 | 1.21708500 |
| H | 5.03513800 | 5.83710300 | 0.42400600 |
| H | 4.87034200 | 5.04858800 | 1.99687600 |
| H | 3.89754200 | 6.50451900 | 1.63296000 |
| H | 1.34358300 | 0.98304000 | 1.95841700 |
| O | -3.35464700 | -1.01259800 | -0.08087600 |
| Si | -4.99693000 | -1.47419200 | -0.23439100 |
| C | -5.81182700 | -1.47199200 | 1.46561100 |
| H | -5.90264100 | -0.45684700 | 1.87047100 |
| H | -6.82802100 | -1.88191300 | 1.39620600 |
| H | -5.26314800 | -2.07780000 | 2.19676300 |
| C | -4.92834800 | -3.22656100 | -0.99776100 |
| C | -4.39773100 | -4.23732200 | 0.04119800 |
| H | -4.31330800 | -5.23905800 | -0.40598200 |
| H | -3.40348400 | -3.96148300 | 0.41451400 |
| H | -5.06486600 | -4.32342700 | 0.90790100 |
| C | -6.35049100 | -3.64868900 | -1.42976800 |
| H | -6.74852500 | -3.00243500 | -2.22170800 |
| H | -6.33768200 | -4.67598300 | -1.82348600 |
| H | -7.06364200 | -3.63270700 | -0.59511400 |
| C | -4.00927900 | -3.24035000 | -2.23746600 |
| H | -4.34441900 | -2.53232200 | -3.00620300 |
| H | -2.97198800 | -2.99027400 | -1.98507800 |
| H | -4.00297600 | -4.24006200 | -2.69672700 |
| C | -5.87240100 | -0.26092000 | -1.38130800 |
| H | -5.81042000 | 0.76436700 | -0.99745300 |
| H | -5.44539600 | -0.26645700 | -2.39164900 |
| H | -6.93761100 | -0.51071800 | -1.47003300 |



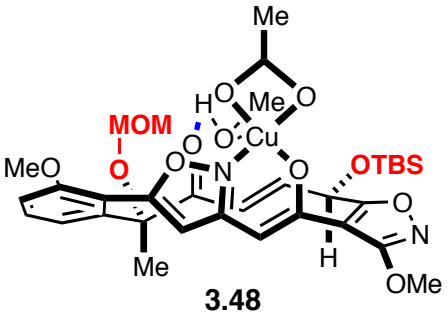



Enolate **3.47**
Free energy: -1745966.642 kcal

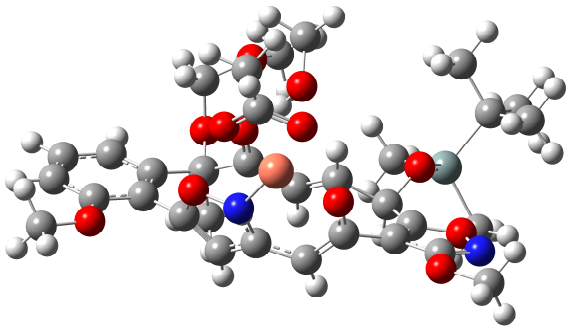
| | | | |
|---|---|---|---|
| H | 0.52532500 | 5.59075600 | 1.63402500 |
| C | 1.16969200 | 5.13445700 | 0.89359900 |
| C | 2.90049900 | 4.03508400 | -0.99686100 |
| C | 0.93011500 | 3.82604700 | 0.45519600 |
| C | 2.24288400 | 5.87610200 | 0.39855400 |
| C | 3.11118300 | 5.34292300 | -0.54872600 |
| C | 1.81499300 | 3.27358000 | -0.50649900 |
| H | 2.40328100 | 6.88920200 | 0.75688100 |
| H | 3.93634500 | 5.93442900 | -0.92641000 |
| C | -0.33116400 | 3.07968000 | 0.94427700 |
| O | -1.28737500 | 3.06338900 | -0.14510200 |
| C | -2.07555600 | 4.19337000 | -0.38626100 |
| H | -2.28956900 | 4.19675900 | -1.46351200 |
| H | -1.55946500 | 5.12659800 | -0.11828300 |
| C | -0.93495600 | 3.66357800 | 2.23968300 |
| H | -1.29267000 | 4.68656500 | 2.10743700 |
| H | -0.18043500 | 3.65445100 | 3.03115400 |
| H | -1.78437000 | 3.05280900 | 2.55986600 |
| C | -0.07486800 | 1.59211600 | 1.32623100 |
| C | -1.14828600 | 0.62854300 | 1.02591200 |
| C | -1.07842000 | -0.68246300 | 1.31214100 |
| C | -2.18793200 | -1.65639600 | 0.97457500 |
| C | -1.67706500 | -2.97937900 | 0.44263400 |
| C | -0.59144600 | -3.37678400 | -0.28681700 |

| | | | |
|---|---|---|---|
| C | -0.75834900 | -4.79804900 | -0.37281400 |
| O | 0.10049200 | -5.60154000 | -1.00315800 |
| C | -0.23307000 | -7.00499800 | -1.03521700 |
| H | -1.18282200 | -7.15863600 | -1.55660100 |
| H | -0.29562900 | -7.40585700 | -0.01900100 |
| N | -1.85989300 | -5.21958500 | 0.21225500 |
| O | -2.44539900 | -4.05194400 | 0.74561200 |
| C | 0.53955900 | -2.53277400 | -0.73250300 |
| C | 1.08822700 | -0.22175100 | -1.36152300 |
| N | 2.34518500 | -0.25494500 | -0.91539800 |
| O | 2.73850600 | 1.05736600 | -0.63453800 |
| C | 1.69272400 | 1.87704400 | -0.95013500 |
| C | 0.67513300 | 1.14346700 | -1.47589600 |
| O | 3.68362700 | 3.41303800 | -1.91950700 |
| C | 4.79939700 | 4.12318900 | -2.46691700 |
| H | 5.52049400 | 4.38976700 | -1.68620900 |
| H | 4.47257800 | 5.02541500 | -2.99621100 |
| O | 0.95638000 | 1.32128200 | 1.94958400 |
| H | -0.22879700 | -1.09741900 | 1.85038900 |
| H | -2.00217200 | 1.01386300 | 0.48809200 |
| C | 0.24267400 | -1.36956500 | -1.41608500 |
| H | -0.77596800 | -1.20732600 | -1.74451000 |
| O | -3.28157100 | 4.06276000 | 0.34754000 |
| C | -4.16631900 | 5.15584400 | 0.12199000 |
| H | -5.06050400 | 4.97006700 | 0.72173100 |
| H | -3.71439200 | 6.10846300 | 0.43462000 |
| O | 1.71427900 | -2.91798500 | -0.31767800 |
| H | -0.28524000 | 1.50089800 | -1.80903100 |
| H | -4.45186300 | 5.23017700 | -0.93728600 |
| H | 5.26421300 | 3.43398300 | -3.17397300 |
| H | 0.58001100 | -7.48443100 | -1.58072100 |
| Cu | 3.33541000 | -1.83146200 | -0.29716100 |
| O | 2.26436400 | -1.11175600 | 2.56960500 |
| H | 1.80210000 | -0.30405600 | 2.26205600 |
| C | 2.63871200 | -0.88899600 | 3.92942800 |
| H | 3.34004300 | -0.04849800 | 4.02781000 |
| H | 3.13294700 | -1.79669000 | 4.28814900 |
| H | 1.76426200 | -0.69300200 | 4.56548300 |
| O | 5.24464100 | -1.16110100 | -0.08006100 |
| C | 5.62470800 | -2.36022500 | 0.15739600 |
| O | 4.73620800 | -3.27486600 | 0.15002500 |
| C | 7.06643300 | -2.65778500 | 0.44029400 |
| H | 7.68726900 | -2.26601600 | -0.37264900 |
| H | 7.23319800 | -3.73086400 | 0.55236900 |
| H | 7.36576200 | -2.14226100 | 1.36031700 |
| H | -2.68680000 | -1.90176000 | 1.92680600 |

| | | | |
|---|---|---|---|
| O | -3.10931800 | -1.11164400 | 0.04203200 |
| Si | -4.75663300 | -0.78742800 | 0.35063400 |
| C | -5.40367300 | -0.09984600 | -1.31072400 |
| C | -4.48689800 | 1.03190800 | -1.82389800 |
| H | -4.38286100 | 1.85169900 | -1.10149000 |
| H | -4.90086100 | 1.46382800 | -2.74761400 |
| H | -3.48033400 | 0.66509400 | -2.05756800 |
| C | -5.45708100 | -1.22157500 | -2.36967600 |
| H | -5.80939400 | -0.82242700 | -3.33264500 |
| H | -6.14318800 | -2.02755800 | -2.08141700 |
| H | -4.47081200 | -1.67012300 | -2.54430500 |
| C | -6.82562100 | 0.46534800 | -1.09843600 |
| H | -6.83416100 | 1.30231100 | -0.38898700 |
| H | -7.52554000 | -0.29444500 | -0.72686300 |
| H | -7.23057200 | 0.84028100 | -2.05018800 |
| C | -5.61122800 | -2.38987200 | 0.86012900 |
| H | -6.69646800 | -2.24471200 | 0.94242400 |
| H | -5.25853100 | -2.73612800 | 1.84004800 |
| H | -5.43668800 | -3.19792000 | 0.14019800 |
| C | -4.88781600 | 0.47456700 | 1.74616900 |
| H | -4.32857500 | 0.14338700 | 2.63115000 |
| H | -5.93242500 | 0.60452100 | 2.05777900 |
| H | -4.49958800 | 1.45859600 | 1.45735500 |




**3.48**



Enolate **3.48**
Free energy: -1745962.674 kcal

| | | | |
|---|---|---|---|
| H | 3.62867500 | -4.78920400 | -0.17506900 |
| C | 4.08027400 | -3.83768300 | -0.42889800 |
| C | 5.28351100 | -1.41183400 | -1.09182100 |
| C | 3.25550400 | -2.73575100 | -0.69860300 |
| C | 5.46721700 | -3.72733600 | -0.48277600 |
| C | 6.08388200 | -2.52137600 | -0.81232400 |

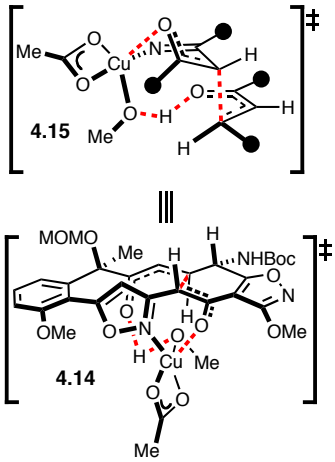
| | | | |
|---|---|---|---|
| C | 3.87200400 | -1.51150000 | -1.04521200 |
| H | 6.08243000 | -4.59635600 | -0.26550800 |
| H | 7.16449600 | -2.45481000 | -0.85007400 |
| C | 1.72504900 | -2.98907500 | -0.70042100 |
| O | 1.39001000 | -4.10281300 | 0.16795300 |
| C | 1.55675200 | -3.99858100 | 1.57874100 |
| H | 2.33204100 | -3.27808300 | 1.84192500 |
| H | 1.84223900 | -5.00756200 | 1.90368900 |
| C | 1.31790500 | -3.51692500 | -2.08423500 |
| H | 1.95694600 | -4.36779100 | -2.33806400 |
| H | 1.43617700 | -2.75899100 | -2.86200700 |
| H | 0.28130300 | -3.86526600 | -2.07579400 |
| C | 0.87990600 | -1.78020600 | -0.18086600 |
| C | -0.41455800 | -1.46228500 | -0.82322800 |
| C | -1.22133200 | -0.48179200 | -0.37598900 |
| C | -2.57046200 | -0.16984500 | -0.99064900 |
| C | -2.80363000 | 1.31104600 | -1.23522800 |
| C | -2.00302100 | 2.41307600 | -1.34395000 |
| C | -2.93957200 | 3.48323100 | -1.51822900 |
| O | -2.57322800 | 4.75902400 | -1.65854800 |
| C | -3.63251800 | 5.71943600 | -1.84608800 |
| H | -4.29944700 | 5.72730000 | -0.97855500 |
| H | -4.20185000 | 5.48990600 | -2.75211800 |
| N | -4.18844400 | 3.07021700 | -1.54924600 |
| O | -4.10129100 | 1.67368500 | -1.36034100 |
| C | -0.52798800 | 2.47055100 | -1.20045700 |
| C | 1.51365700 | 1.21721200 | -1.72643900 |
| N | 2.21407700 | 1.65729500 | -0.67947400 |
| O | 3.20157000 | 0.70576500 | -0.39400000 |
| C | 3.08618000 | -0.29604200 | -1.31091300 |
| C | 2.10981200 | 0.00908000 | -2.20733000 |
| O | 5.76724500 | -0.18681400 | -1.43630600 |
| C | 7.18425600 | -0.01071400 | -1.53166700 |
| H | 7.61521000 | -0.67449500 | -2.28989500 |
| H | 7.67144200 | -0.18362400 | -0.56530800 |
| O | 1.29464000 | -1.18015300 | 0.81461600 |
| H | -0.97072400 | 0.07458100 | 0.52443200 |
| H | -0.69064100 | -2.01575900 | -1.71348400 |
| C | 0.22834100 | 1.72206800 | -2.07970000 |
| H | -0.26216900 | 1.26023800 | -2.92718300 |
| O | 0.38799600 | -3.58810300 | 2.23715300 |
| C | -0.67526900 | -4.53813000 | 2.16641600 |
| H | -1.02774000 | -4.67163300 | 1.13717700 |
| H | -0.36027400 | -5.51316100 | 2.56567700 |
| O | -0.09296700 | 3.13821900 | -0.16965400 |
| H | 1.78208100 | -0.57555300 | -3.05258200 |

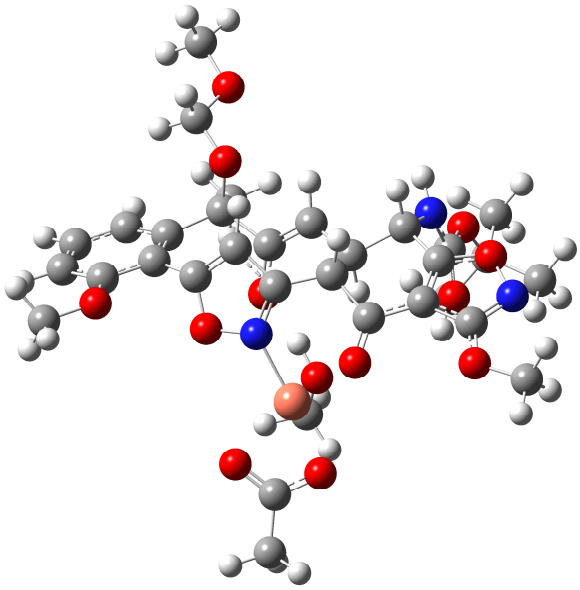
| | | | |
|---|---|---|---|
| H | -1.48918700 | -4.14484900 | 2.78031000 |
| H | 7.33008800 | 1.02857600 | -1.83119000 |
| H | -3.13505600 | 6.68425200 | -1.94810700 |
| Cu | 1.67623200 | 3.00839400 | 0.64007900 |
| H | -2.66098100 | -0.69057000 | -1.95374900 |
| O | -3.56584900 | -0.61548300 | -0.06915200 |
| Si | -4.69416100 | -1.86039200 | -0.36194700 |
| C | -5.83603100 | -1.78749100 | 1.16849200 |
| C | -5.02255200 | -2.07140000 | 2.44924600 |
| H | -4.56324000 | -3.06785000 | 2.43065700 |
| H | -5.67487500 | -2.02936900 | 3.33437400 |
| H | -4.22153500 | -1.33702200 | 2.59877200 |
| C | -6.48352600 | -0.39075700 | 1.27850600 |
| H | -7.12077500 | -0.33394600 | 2.17382500 |
| H | -7.11851900 | -0.16332800 | 0.41297400 |
| H | -5.73290900 | 0.40486200 | 1.35773300 |
| C | -6.94781600 | -2.84999500 | 1.02813200 |
| H | -6.54359800 | -3.86870100 | 0.96915100 |
| H | -7.56629500 | -2.68345000 | 0.13712400 |
| H | -7.61918700 | -2.81770600 | 1.89920300 |
| C | -5.61290400 | -1.50361800 | -1.96953000 |
| H | -6.14867100 | -0.54786200 | -1.93887600 |
| H | -6.34549500 | -2.29332300 | -2.18128900 |
| H | -4.92422300 | -1.46994900 | -2.82381800 |
| C | -3.78910300 | -3.50764200 | -0.50565600 |
| H | -3.16762300 | -3.71562500 | 0.37322100 |
| H | -3.13455700 | -3.52559000 | -1.38674700 |
| H | -4.49966100 | -4.33703400 | -0.61876100 |
| O | 0.41434300 | 0.89976400 | 2.51022700 |
| H | 0.76862600 | 0.28063000 | 1.83981800 |
| C | 0.15751700 | 0.12944900 | 3.68573900 |
| H | 1.08874800 | -0.19004600 | 4.17524900 |
| H | -0.44270700 | -0.76266600 | 3.46268500 |
| H | -0.40088300 | 0.76272100 | 4.38157700 |
| O | 1.47649500 | 4.35882500 | 2.17021000 |
| C | 2.63747400 | 4.02038900 | 2.58068200 |
| O | 3.27263000 | 3.14149500 | 1.90278100 |
| C | 3.23594500 | 4.64584100 | 3.80445600 |
| H | 4.14179100 | 4.11859900 | 4.11067700 |
| H | 2.50346800 | 4.64156100 | 4.61786800 |
| H | 3.48295800 | 5.69174700 | 3.58538600 |

*Comparison of restricted vs. unrestricted B3LYP*

| | free energy (hartrees) | | |
|---|---|---|---|
| **Conformer** | **rb3lyp** | **ub3lyp** | **difference (kcal)** |
| NHBoc_CuEnolate_1 | -2581.7399 | -2581.7400 | 0.04 |
| NHBoc_CuEnolate_2 | -2581.7331 | -2581.7334 | 0.14 |
| NHBoc_CuEnolate_3 | -2581.7518 | -2581.7518 | 0.00 |
| NHBoc_CuEnolate_4 | -2581.7483 | -2581.7483 | 0.00 |
| NHBoc_CuEnolate_5 | -2581.7475 | -2581.7475 | 0.00 |
| NHBoc_CuEnolate_6 | -2581.7315 | -2581.7315 | 0.00 |
| NHBoc_CuEnolate_7 | -2581.7449 | -2581.7448 | -0.05 |
| NHBoc_CuEnolate_8 | -2581.7503 | -2581.7503 | 0.00 |
| NHBoc_CuEnolate_9 | -2581.7461 | -2581.7452 | -0.57 |
| NHBoc_CuEnolate_10 | -2581.7453 | -2581.7453 | 0.00 |
| NHBoc_CuEnolate_11 | -2581.7475 | -2581.7475 | 0.00 |
| NHBoc_CuEnolate_12 | -2581.7457 | -2581.7459 | 0.15 |
| NHBoc_CuEnolate_13 | -2581.7479 | -2581.7479 | 0.00 |
| NHBoc_CuEnolate_14 | -2581.7329 | -2581.7328 | 0.00 |
| NHBoc_CuEnolate_15 | -2581.7356 | -2581.7356 | -0.02 |
| NHBoc_CuEnolate_16 | -2581.7467 | -2581.7467 | 0.00 |
| NHBoc_CuEnolate_17 | -2581.7390 | -2581.7394 | 0.23 |
| NHBoc_CuEnolate_18 | -2581.7474 | -2581.7471 | -0.20 |
| NHBoc_CuEnolate_19 | -2581.7435 | -2581.7428 | -0.39 |
| NHBoc_CuEnolate_20 | -2581.7434 | -2581.7434 | 0.00 |

*transition state calculations*



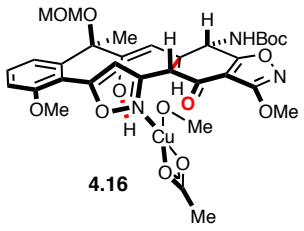



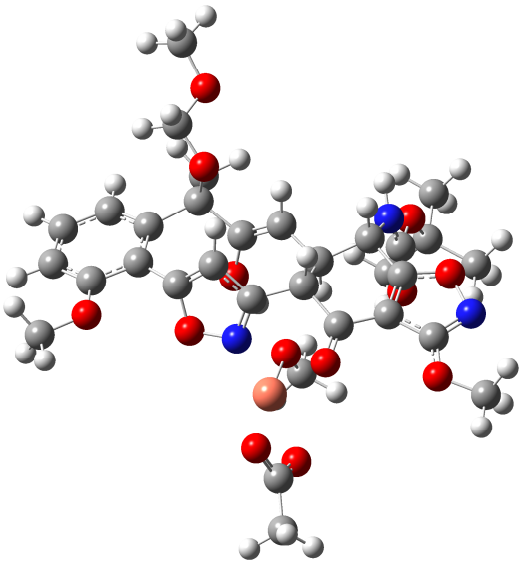
Transition state structure **4.14**
Free energy: -1620050.093 kcal

| | | | |
|---|---|---|---|
| H | 4.96541500 | 2.53530300 | 1.53533000 |
| C | 4.99862900 | 1.57396500 | 1.04010800 |
| C | 5.18992800 | -0.93331600 | -0.14956200 |
| C | 3.88676500 | 1.11092700 | 0.31977000 |
| C | 6.16816100 | 0.82062000 | 1.15446200 |
| C | 6.28540700 | -0.43077400 | 0.55770700 |
| C | 4.00516500 | -0.17642900 | -0.27759200 |
| H | 7.00556900 | 1.22012500 | 1.72027000 |
| H | 7.20182500 | -1.00075500 | 0.65405800 |
| C | 2.66600900 | 2.07074000 | 0.12469500 |
| O | 2.79758600 | 2.64543000 | -1.21042200 |
| C | 3.76770400 | 3.62502300 | -1.43655200 |
| H | 4.08178000 | 3.51761200 | -2.48513700 |
| H | 4.64694600 | 3.50335900 | -0.78748100 |
| C | 2.59064100 | 3.17011000 | 1.20032400 |
| H | 1.71504700 | 3.79399400 | 0.99957500 |
| H | 2.46686200 | 2.70810100 | 2.18426500 |
| H | 3.46609400 | 3.82230500 | 1.22917100 |
| C | 1.28101300 | 1.35073900 | 0.17921200 |
| C | 0.31505300 | 1.63592400 | -0.76377000 |
| C | -0.88389900 | 0.77893700 | -0.94033000 |
| C | -2.08882300 | 1.51503600 | -1.60142600 |
| H | -1.74954300 | 1.93231300 | -2.55809200 |
| C | -3.16496000 | 0.50779000 | -1.89001300 |
| C | -3.03145400 | -0.85718900 | -1.94306600 |
| C | -4.37688900 | -1.31754200 | -2.13302800 |
| O | -4.71574700 | -2.59816400 | -2.22236500 |
| C | -6.12093900 | -2.88443600 | -2.40761900 |
| H | -6.69979400 | -2.48778600 | -1.56865500 |
| H | -6.19157200 | -3.97150200 | -2.43803400 |
| N | -5.23210400 | -0.32184200 | -2.23473300 |
| O | -4.43842900 | 0.85554600 | -2.06493900 |
| C | -1.76346100 | -1.50059600 | -1.68352400 |
| C | 0.75796500 | -1.07504100 | -1.57423600 |
| N | 0.99341900 | -2.01713200 | -0.67845200 |
| O | 2.30037400 | -1.88349700 | -0.25110800 |
| C | 2.84074400 | -0.80895600 | -0.90938100 |
| C | 1.95526700 | -0.36236300 | -1.84028800 |
| O | 5.16588300 | -2.15177000 | -0.76016800 |
| C | 6.33776100 | -2.97073600 | -0.70148900 |
| H | 6.08804500 | -3.87891800 | -1.25311300 |
| H | 6.58909600 | -3.22944100 | 0.33330400 |
| O | 1.17844200 | 0.52139500 | 1.16951600 |
| H | -1.21909000 | 0.37597300 | 0.01791300 |
| H | 0.56324600 | 2.31706000 | -1.57007900 |

| | | | |
|---|---|---|---|
| C | -3.19578000 | 2.47188000 | 0.38630500 |
| O | -3.56212900 | 1.37981500 | 0.81704700 |
| O | -3.35067600 | 3.66209100 | 0.99102500 |
| C | -4.04267900 | 3.79860500 | 2.29777200 |
| C | -3.96831000 | 5.30561900 | 2.54730000 |
| H | -2.92664800 | 5.64166800 | 2.59413400 |
| H | -4.47669200 | 5.85939300 | 1.75034800 |
| H | -4.45187000 | 5.54890900 | 3.49904800 |
| C | -3.27468500 | 3.03362800 | 3.37760600 |
| H | -3.71752500 | 3.24857700 | 4.35667500 |
| H | -3.30875500 | 1.95449600 | 3.21440300 |
| H | -2.22678800 | 3.35322000 | 3.40141700 |
| C | -5.49689000 | 3.34223300 | 2.16361500 |
| H | -5.98844000 | 3.86688400 | 1.33643500 |
| H | -5.57182900 | 2.26650100 | 1.99034800 |
| H | -6.03900400 | 3.58018600 | 3.08577300 |
| N | -2.59348900 | 2.63950700 | -0.82967800 |
| H | -2.18316600 | 3.54538700 | -1.01908200 |
| C | -0.60179700 | -0.56220200 | -1.89147500 |
| H | -0.61975600 | -0.19600700 | -2.92334300 |
| O | 3.18475700 | 4.90391000 | -1.24111100 |
| C | 4.12992200 | 5.94912200 | -1.43267700 |
| H | 4.95397700 | 5.88831700 | -0.70605300 |
| H | 3.59690100 | 6.89274900 | -1.28888600 |
| O | -1.67273200 | -2.66556500 | -1.24762200 |
| H | 2.08460700 | 0.46830800 | -2.51183800 |
| H | 4.55375000 | 5.92995800 | -2.44799800 |
| H | 7.19083100 | -2.47602000 | -1.17980200 |
| H | -6.47483500 | -2.45224600 | -3.34805800 |
| Cu | -0.24441700 | -3.11448300 | 0.38958000 |
| O | -0.61092800 | -1.34270900 | 1.69059700 |
| H | 0.03357400 | -0.61059500 | 1.42056000 |
| C | -0.48272300 | -1.53262300 | 3.10389300 |
| H | 0.50788600 | -1.92257100 | 3.37141800 |
| H | -1.24528700 | -2.24849600 | 3.42068400 |
| H | -0.64698900 | -0.58470200 | 3.63137700 |
| O | 0.86540400 | -4.55079300 | 1.57446100 |
| C | -0.27628100 | -4.97425900 | 1.92687800 |
| O | -1.31389100 | -4.40771400 | 1.41478500 |
| C | -0.44272300 | -6.07774800 | 2.92827400 |
| H | -0.59878000 | -5.63239100 | 3.91905100 |
| H | 0.45248000 | -6.70301100 | 2.96533600 |
| H | -1.32056600 | -6.68392100 | 2.68806300 |

*Ground-state following Michael addition*



Michael product – copper complex **4.16**
Free energy: -1620058.563 kcal

| | | | |
|---|---|---|---|
| H | 5.36973300 | 1.94397900 | 1.39275700 |
| C | 5.24362900 | 0.92776000 | 1.04390000 |
| C | 5.01829500 | -1.72509400 | 0.23510200 |
| C | 4.07934100 | 0.55402800 | 0.35570000 |
| C | 6.26600800 | 0.01478700 | 1.30791700 |
| C | 6.17405900 | -1.31330000 | 0.90458200 |
| C | 3.98405800 | -0.80824300 | -0.04971800 |
| H | 7.15245500 | 0.34871600 | 1.84039000 |
| H | 6.97809900 | -2.00750800 | 1.11794100 |
| C | 3.03734200 | 1.67008400 | -0.00718300 |
| O | 3.23194700 | 1.99883900 | -1.40907500 |
| C | 4.34670700 | 2.75301900 | -1.78922600 |
| H | 4.60100700 | 2.43250000 | -2.80970100 |
| H | 5.21254900 | 2.58060200 | -1.13391700 |
| C | 3.16268400 | 2.92067800 | 0.88454600 |
| H | 2.40027200 | 3.64240200 | 0.57951400 |
| H | 2.98813800 | 2.65107800 | 1.93038700 |
| H | 4.13580600 | 3.40889500 | 0.80774900 |
| C | 1.56686700 | 1.20952900 | 0.10307900 |
| C | 0.64844400 | 1.44915900 | -0.85789900 |
| C | -0.67407000 | 0.74835800 | -0.99045700 |
| C | -1.76628200 | 1.66208200 | -1.61861100 |
| H | -1.40423400 | 2.01695500 | -2.59230900 |
| C | -2.98117600 | 0.82050900 | -1.86489100 |
| C | -3.02112100 | -0.54066600 | -2.00674500 |

| | | | |
|---|---|---|---|
| C | -4.41546200 | -0.80882200 | -2.22012400 |
| O | -4.91925000 | -2.02477900 | -2.40024900 |
| C | -6.35090300 | -2.11137300 | -2.58178000 |
| H | -6.86761700 | -1.71891900 | -1.70117200 |
| H | -6.56126600 | -3.17373300 | -2.70501100 |
| N | -5.14003600 | 0.29057800 | -2.22144000 |
| O | -4.19946100 | 1.34321700 | -1.98916700 |
| C | -1.84214100 | -1.38406000 | -1.92110700 |
| C | 0.67453700 | -1.31668900 | -1.40601100 |
| N | 0.67034400 | -2.08539700 | -0.33192000 |
| O | 1.97255400 | -2.12851000 | 0.15124000 |
| C | 2.74393800 | -1.32616000 | -0.64752000 |
| C | 2.00089100 | -0.90934500 | -1.70518900 |
| O | 4.79060000 | -2.99955100 | -0.18945300 |
| C | 5.80020800 | -3.98871100 | 0.03492300 |
| H | 5.40525300 | -4.91185400 | -0.39285800 |
| H | 5.98393900 | -4.13203800 | 1.10577800 |
| O | 1.38751000 | 0.54414400 | 1.26688600 |
| H | -1.03554700 | 0.41411600 | -0.01554200 |
| H | 0.99418000 | 1.99133300 | -1.73124000 |
| C | -2.63457300 | 2.80420400 | 0.39358700 |
| O | -3.11828400 | 1.78263800 | 0.87908100 |
| O | -2.60399900 | 4.02372800 | 0.95824600 |
| C | -3.23892700 | 4.30958700 | 2.26885000 |
| C | -2.93874100 | 5.79810900 | 2.45209600 |
| H | -1.85831300 | 5.97969700 | 2.46427200 |
| H | -3.38155800 | 6.38681400 | 1.64117400 |
| H | -3.35825200 | 6.14878200 | 3.40068700 |
| C | -2.57086300 | 3.48080100 | 3.36759100 |
| H | -2.92600600 | 3.82399600 | 4.34590600 |
| H | -2.80275500 | 2.41807400 | 3.27245600 |
| H | -1.48302000 | 3.61034700 | 3.33729900 |
| C | -4.74621000 | 4.06701300 | 2.17677200 |
| H | -5.17579600 | 4.63130600 | 1.34137000 |
| H | -4.97929100 | 3.00831100 | 2.04261900 |
| H | -5.22520000 | 4.41066100 | 3.10046500 |
| N | -2.06298000 | 2.85432800 | -0.84553000 |
| H | -1.58525000 | 3.70779200 | -1.10503600 |
| C | -0.53791600 | -0.58361200 | -1.89322900 |
| H | -0.34999200 | -0.25742000 | -2.92542500 |
| O | 3.99071200 | 4.12434300 | -1.79170800 |
| C | 5.04838100 | 4.94446900 | -2.27413200 |
| H | 5.94818800 | 4.85850300 | -1.64712300 |
| H | 4.69066600 | 5.97680600 | -2.24517800 |
| O | -1.87867200 | -2.61322700 | -1.90614900 |
| H | 2.30940500 | -0.24256000 | -2.49312600 |

| | | | |
|---|---|---|---|
| H | 5.31678700 | 4.68669000 | -3.30978600 |
| H | 6.73492600 | -3.72190600 | -0.47115300 |
| H | -6.65427800 | -1.55708200 | -3.47478900 |
| Cu | -0.73474500 | -2.62302600 | 1.06094600 |
| O | -0.73819700 | -0.86720200 | 1.78475000 |
| H | 0.48711100 | 0.08266500 | 1.39570400 |
| C | -1.33729300 | -0.62965200 | 3.04284000 |
| H | -0.91342900 | -1.26265800 | 3.83952900 |
| H | -2.42519100 | -0.79787600 | 3.02360000 |
| H | -1.16700100 | 0.41801200 | 3.33372600 |
| O | -0.92989500 | -4.61639100 | 0.56542500 |
| C | -1.79932300 | -4.74305900 | 1.49172600 |
| O | -2.09125400 | -3.71069800 | 2.18447100 |
| C | -2.43247100 | -6.07282400 | 1.77977800 |
| H | -1.75225700 | -6.65644200 | 2.41308700 |
| H | -2.58908800 | -6.62959600 | 0.85168600 |
| H | -3.37886400 | -5.94605200 | 2.31067700 |

## II. Geometries and Energies Relevant to Chapter 5

For each molecule, the geometries and energies corresponding to the lowest energy "correct" and "incorrect" diastereofaces to the periphery are given. DFT structures were verified to be true local minima by standard frequency analyses. Molecules are listed in order of their appearance in the manuscript. Numbering refers to the starting material being considered. Free energies are given at 298.15 K in all cases, regardless of the temperature at which the reaction was performed.

Compound **5.7**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +84.153175 kJ.

| | | | |
|---|---|---|---|
| H | -0.25100 | -0.51960 | 1.49190 |
| C | -0.28080 | -1.53450 | 1.89130 |
| C | -0.32950 | -2.50800 | 0.69890 |
| H | -1.21040 | -1.59290 | 2.45950 |
| C | -0.90620 | -3.86560 | 1.06430 |
| C | -0.29570 | -5.05000 | 1.28410 |
| C | 1.14800 | -5.36510 | 1.29750 |
| C | 2.22680 | -4.33870 | 1.71950 |
| C | 3.64650 | -4.85440 | 1.39950 |
| C | 2.14080 | -3.94530 | 3.21510 |
| H | 2.11640 | -3.44830 | 1.11490 |
| H | 3.06880 | -3.44740 | 3.49910 |
| H | 2.10460 | -4.85030 | 3.82400 |
| C | 0.97650 | -3.01940 | 3.62170 |
| H | 0.02160 | -3.54110 | 3.57860 |
| C | 0.92530 | -1.69160 | 2.83810 |
| H | 1.10460 | -2.78450 | 4.67940 |
| H | 1.85550 | -1.52390 | 2.29380 |
| H | 0.87800 | -0.87680 | 3.56210 |

| | | | |
|---|---|---|---|
| O | 1.51060 | -6.50330 | 1.00270 |
| H | 4.39660 | -4.08520 | 1.58270 |
| H | 3.73530 | -5.14820 | 0.35260 |
| H | 3.90320 | -5.72230 | 2.00860 |
| H | -0.93190 | -5.89460 | 1.50320 |
| H | -1.98360 | -3.86410 | 1.14750 |
| H | 0.61890 | -2.57180 | 0.17320 |
| H | -1.01080 | -2.09400 | -0.04580 |

---

Compound **5.7**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +87.738075 kJ.

| | | | |
|---|---|---|---|
| H | -1.17220 | -1.19020 | 1.87380 |
| C | -0.63940 | -1.96010 | 2.43380 |
| C | -1.11750 | -3.32920 | 1.91860 |
| H | -0.94980 | -1.83160 | 3.47160 |
| C | -0.63940 | -3.63240 | 0.50720 |
| C | 0.37030 | -4.45140 | 0.15040 |
| C | 1.20150 | -5.18500 | 1.11490 |
| C | 2.35600 | -4.44110 | 1.81290 |
| C | 3.60770 | -5.33670 | 1.89550 |
| C | 1.94880 | -3.91110 | 3.21210 |
| H | 2.61710 | -3.59540 | 1.17760 |
| H | 2.70360 | -4.20890 | 3.94090 |
| H | 1.04710 | -4.40380 | 3.57260 |
| C | 1.79690 | -2.37910 | 3.31880 |
| H | 1.47090 | -2.12780 | 4.32910 |
| C | 0.87260 | -1.67720 | 2.30200 |
| H | 2.79090 | -1.94040 | 3.22070 |
| H | 1.21480 | -1.85010 | 1.28250 |
| H | 1.00540 | -0.60460 | 2.45060 |
| O | 1.00500 | -6.37260 | 1.36660 |
| H | 3.87320 | -5.73850 | 0.91690 |
| H | 3.44890 | -6.18290 | 2.56570 |
| H | 4.46700 | -4.77620 | 2.26360 |
| H | 0.60470 | -4.59060 | -0.89380 |
| H | -1.17530 | -3.11800 | -0.27710 |
| H | -2.20800 | -3.34890 | 1.91030 |
| H | -0.83790 | -4.12430 | 2.60530 |

---

Compound **5.7**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -465.901165894 hartree.
Free Energy: -465.694043 hartree.

| | | | |
|---|---|---|---|
| H | -0.40966 | -0.50278 | 1.62629 |
| C | -0.35318 | -1.54763 | 1.95857 |
| C | -0.31164 | -2.43971 | 0.68983 |
| H | -1.28577 | -1.74167 | 2.50603 |
| C | -0.85395 | -3.83425 | 0.88579 |
| C | -0.27045 | -5.00976 | 1.18698 |
| C | 1.13459 | -5.38539 | 1.49942 |
| C | 2.24774 | -4.35251 | 1.69574 |
| C | 3.61008 | -4.96610 | 1.34213 |
| C | 2.24760 | -3.85068 | 3.16505 |
| H | 2.07346 | -3.49666 | 1.03748 |
| H | 3.15523 | -3.24582 | 3.30073 |
| H | 2.36344 | -4.72713 | 3.81668 |
| C | 1.04066 | -3.02353 | 3.64399 |
| H | 0.12265 | -3.61871 | 3.58521 |
| C | 0.84310 | -1.66554 | 2.92150 |
| H | 1.19774 | -2.83263 | 4.71317 |
| H | 1.76190 | -1.40037 | 2.37823 |
| H | 0.71636 | -0.87862 | 3.67599 |
| O | 1.37656 | -6.57634 | 1.66517 |
| H | 4.40593 | -4.22418 | 1.47223 |
| H | 3.63122 | -5.31254 | 0.30331 |
| H | 3.82405 | -5.82783 | 1.97986 |
| H | -0.91498 | -5.88561 | 1.24286 |
| H | -1.93680 | -3.88686 | 0.75795 |
| H | 0.70272 | -2.44394 | 0.28126 |
| H | -0.94049 | -1.96411 | -0.07344 |

---

Compound **5.7**.
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -465.909364382 hartree.
Free Energy: -465.703773 hartree.

| | | | |
|---|---|---|---|
| H | -0.77392 | -0.94569 | 1.44731 |
| C | -0.45040 | -1.69569 | 2.18218 |
| C | -1.12374 | -3.04297 | 1.82210 |
| H | -0.84239 | -1.36126 | 3.15303 |
| C | -0.63521 | -3.61814 | 0.51889 |
| C | 0.25400 | -4.60623 | 0.36914 |
| C | 0.92797 | -5.39262 | 1.46472 |
| C | 2.12498 | -4.77174 | 2.19911 |
| C | 3.12990 | -5.86570 | 2.58628 |
| C | 1.65190 | -3.96880 | 3.45953 |
| H | 2.61122 | -4.07381 | 1.50590 |
| H | 2.27101 | -4.29537 | 4.30468 |
| H | 0.63120 | -4.25633 | 3.73294 |
| C | 1.77883 | -2.43529 | 3.37142 |
| H | 1.42144 | -2.01506 | 4.32296 |
| C | 1.08745 | -1.69442 | 2.21234 |
| H | 2.85015 | -2.19233 | 3.32078 |
| H | 1.46437 | -2.07369 | 1.25360 |
| H | 1.41501 | -0.64706 | 2.26431 |
| O | 0.55198 | -6.52867 | 1.71180 |
| H | 3.48198 | -6.41955 | 1.70818 |
| H | 2.67652 | -6.58575 | 3.27448 |
| H | 4.00213 | -5.41948 | 3.07756 |
| H | 0.51663 | -4.94686 | -0.63366 |
| H | -1.04493 | -3.16527 | -0.38512 |
| H | -2.20655 | -2.87298 | 1.75039 |
| H | -0.98424 | -3.76624 | 2.63095 |

---

Compound **5.7**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -465.691970109 hartree.
Free Energy: -465.482344 hartree.

| | | | |
|---|---|---|---|
| H | -0.79495 | -0.83751 | 2.16737 |
| C | -0.20161 | -1.73036 | 1.94371 |
| C | -1.12424 | -2.71687 | 1.18789 |
| H | 0.60211 | -1.39579 | 1.27370 |
| C | -0.38196 | -3.63642 | 0.25126 |
| C | 0.31276 | -4.71592 | 0.61381 |
| C | 0.44579 | -5.14206 | 2.04322 |
| C | 1.85050 | -5.03189 | 2.62308 |
| C | 1.88446 | -5.47465 | 4.08024 |
| C | 2.45207 | -3.62687 | 2.39241 |
| H | 2.45808 | -5.72593 | 2.02094 |
| H | 2.32237 | -3.34942 | 1.34015 |
| H | 3.53374 | -3.69937 | 2.55915 |
| C | 1.90940 | -2.51515 | 3.29574 |
| H | 2.19777 | -2.73290 | 4.33196 |
| C | 0.39652 | -2.25968 | 3.27052 |
| H | 2.42726 | -1.58365 | 3.03070 |
| H | 0.19418 | -1.51907 | 4.05314 |
| H | -0.13833 | -3.16297 | 3.58560 |
| O | -0.50269 | -5.53345 | 2.69546 |
| H | 1.56453 | -6.51530 | 4.17972 |
| H | 1.21131 | -4.86719 | 4.69287 |
| H | 2.89773 | -5.38367 | 4.48529 |
| H | 0.91282 | -5.25788 | -0.11601 |
| H | -0.35679 | -3.34237 | -0.79768 |
| H | -1.84950 | -2.14467 | 0.60141 |
| H | -1.69563 | -3.30157 | 1.91623 |

---

Compound **5.7**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -465.695043779 hartree.
Free Energy: -465.485226 hartree.

| | | | |
|---|---|---|---|
| H | 3.32103 | 0.46131 | 0.65398 |
| C | 2.59996 | -0.14868 | 0.09512 |
| C | 1.71400 | -0.88865 | 1.11635 |
| H | 3.18209 | -0.88341 | -0.47453 |
| C | 0.86412 | -1.94557 | 0.46737 |
| C | -0.27790 | -1.83022 | -0.22591 |
| C | -1.06189 | -0.61120 | -0.56725 |
| C | -1.14976 | 0.60775 | 0.35009 |
| C | -2.63896 | 0.89804 | 0.57923 |
| C | -0.46805 | 1.83393 | -0.28827 |
| H | -0.69074 | 0.38489 | 1.31674 |
| H | -0.88648 | 2.73130 | 0.18415 |
| H | -0.76749 | 1.86927 | -1.34417 |
| C | 1.05821 | 1.89766 | -0.17458 |
| H | 1.37791 | 2.85854 | -0.59276 |
| C | 1.83117 | 0.75635 | -0.87054 |
| H | 1.33192 | 1.93384 | 0.88915 |
| H | 2.55443 | 1.18065 | -1.57588 |

| | | | |
|---|---|---|---|
| H | 1.15222 | 0.15182 | -1.48518 |
| O | -1.70128 | -0.61406 | -1.60640 |
| H | -3.15939 | 0.02632 | 0.98929 |
| H | -3.11978 | 1.16602 | -0.36587 |
| H | -2.75702 | 1.72869 | 1.28174 |
| H | -0.66808 | -2.71781 | -0.72081 |
| H | 1.29230 | -2.94755 | 0.49841 |
| H | 2.36121 | -1.37267 | 1.85451 |
| H | 1.11422 | -0.15708 | 1.66389 |

---

Compound **5.7**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -465.914893515 hartree.
Free Energy: -465.707575 hartree.

| | | | |
|---|---|---|---|
| H | -0.18113 | -0.61740 | 2.02610 |
| C | -0.48518 | -1.67228 | 2.06984 |
| C | -0.13795 | -2.31423 | 0.70289 |
| H | -1.57571 | -1.67527 | 2.20070 |
| C | -0.70187 | -3.70092 | 0.55067 |
| C | -0.24637 | -4.88784 | 0.99763 |
| C | 0.96065 | -5.23535 | 1.79269 |
| C | 2.24839 | -4.39978 | 1.78556 |
| C | 3.43410 | -5.34971 | 1.53028 |
| C | 2.44881 | -3.64275 | 3.12681 |
| H | 2.21589 | -3.67788 | 0.96494 |
| H | 3.52480 | -3.45189 | 3.23603 |
| H | 2.17606 | -4.32056 | 3.94680 |
| C | 1.72109 | -2.29666 | 3.29569 |
| H | 2.06479 | -1.86911 | 4.24619 |
| C | 0.17112 | -2.33209 | 3.29272 |
| H | 2.07531 | -1.60225 | 2.52029 |
| H | -0.20398 | -1.81086 | 4.18271 |
| H | -0.18742 | -3.36434 | 3.39139 |
| O | 0.92580 | -6.27133 | 2.45315 |
| H | 3.30570 | -5.91053 | 0.59690 |
| H | 3.53453 | -6.07305 | 2.34512 |
| H | 4.36591 | -4.77789 | 1.45483 |
| H | -0.89226 | -5.75478 | 0.86302 |
| H | -1.67890 | -3.73368 | 0.06641 |
| H | -0.55837 | -1.68304 | -0.08881 |
| H | 0.94708 | -2.29713 | 0.56695 |

---

Compound **5.7**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -465.897479863 hartree.
Free Energy: -465.690272 hartree.

| | | | |
|---|---|---|---|
| H | -0.68212 | -1.21747 | 1.85740 |
| C | -0.85276 | -2.13159 | 2.44382 |
| C | -1.36919 | -3.26829 | 1.52276 |
| H | -1.66695 | -1.89549 | 3.14125 |
| C | -0.52717 | -3.49444 | 0.29218 |
| C | 0.58467 | -4.24028 | 0.21222 |
| C | 1.20451 | -4.95365 | 1.36865 |
| C | 2.67105 | -4.60204 | 1.64021 |
| C | 3.47690 | -5.84039 | 2.05228 |
| C | 2.74818 | -3.50039 | 2.73873 |
| H | 3.09397 | -4.17572 | 0.72020 |
| H | 3.78711 | -3.14677 | 2.75243 |
| H | 2.57279 | -3.97488 | 3.71342 |
| C | 1.79139 | -2.29397 | 2.58513 |
| H | 2.28245 | -1.41627 | 3.02235 |
| C | 0.40490 | -2.47361 | 3.27401 |
| H | 1.66454 | -2.05692 | 1.52284 |
| H | 0.39107 | -1.84200 | 4.17119 |
| H | 0.30336 | -3.50144 | 3.64142 |
| O | 0.58315 | -5.70773 | 2.10335 |
| H | 3.53313 | -6.57101 | 1.23748 |
| H | 3.00102 | -6.32795 | 2.90828 |
| H | 4.50007 | -5.56272 | 2.33003 |
| H | 1.16910 | -4.22701 | -0.70739 |
| H | -0.81664 | -2.93098 | -0.59608 |
| H | -2.38808 | -3.01745 | 1.20247 |
| H | -1.43284 | -4.19244 | 2.10387 |

---

Compound **5.8**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +106.444145 kJ.

| | | | |
|---|---|---|---|
| H | 1.69720 | 0.91770 | 6.38210 |

| | | | |
|---|---|---|---|
| C | 1.27200 | 0.00500 | 6.80200 |
| C | 1.69220 | -1.17320 | 5.89690 |
| H | 1.73090 | -0.09980 | 7.78610 |
| C | 0.84880 | -2.37580 | 6.22530 |
| C | -0.20230 | -2.74850 | 5.47820 |
| C | -1.29210 | -3.51610 | 6.07900 |
| C | -1.73600 | -3.13060 | 7.51230 |
| C | -2.91430 | -4.00710 | 7.98650 |
| C | -2.08180 | -1.61380 | 7.65480 |
| H | -0.90530 | -3.36120 | 8.17810 |
| H | -2.84980 | -1.52220 | 8.42400 |
| H | -2.56760 | -1.24230 | 6.75110 |
| C | -0.92150 | -0.66920 | 8.08110 |
| H | -1.33190 | 0.03190 | 8.80980 |
| C | -0.26270 | 0.18950 | 6.96330 |
| H | -0.17230 | -1.22180 | 8.64850 |
| H | -0.44100 | 1.23710 | 7.21080 |
| H | -0.76240 | 0.04740 | 6.00450 |
| O | -1.87080 | -4.40920 | 5.46300 |
| H | -2.67920 | -5.06930 | 7.90230 |
| H | -3.81160 | -3.82050 | 7.39490 |
| H | -3.15570 | -3.81410 | 9.03160 |
| H | -0.39370 | -2.29890 | 4.51580 |
| H | 0.98700 | -2.77700 | 7.21910 |
| H | 1.55520 | -0.90560 | 4.84800 |
| H | 2.74860 | -1.41000 | 6.02930 |

---

Compound **5.8**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +117.006638 kJ.

| | | | |
|---|---|---|---|
| H | 0.15530 | 0.88240 | 6.14330 |
| C | 0.89520 | 0.17160 | 6.51420 |
| C | 1.17890 | -0.90200 | 5.44280 |
| H | 1.80760 | 0.75230 | 6.65700 |
| C | 0.06230 | -1.91260 | 5.43510 |
| C | 0.16180 | -3.10820 | 6.03520 |
| C | -1.04410 | -3.82850 | 6.43800 |
| C | -2.07190 | -3.10970 | 7.33700 |
| C | -3.26270 | -2.54150 | 6.54170 |
| C | -1.47970 | -2.14320 | 8.41250 |
| H | -2.49030 | -3.93400 | 7.91640 |
| H | -0.64120 | -2.62640 | 8.91580 |
| H | -2.23810 | -2.05710 | 9.19180 |
| C | -1.08750 | -0.69410 | 7.99750 |
| H | -1.61420 | -0.38300 | 7.09750 |
| C | 0.43380 | -0.38990 | 7.88600 |
| H | -1.48260 | -0.02590 | 8.76440 |
| H | 1.03620 | -1.25860 | 8.15350 |
| H | 0.67510 | 0.35600 | 8.64490 |
| O | -1.25460 | -4.99090 | 6.10230 |
| H | -3.68670 | -3.30220 | 5.88450 |
| H | -2.99010 | -1.69280 | 5.91760 |
| H | -4.05690 | -2.21710 | 7.21400 |
| H | 1.10190 | -3.46180 | 6.42970 |
| H | -0.89920 | -1.54260 | 5.11160 |
| H | 1.27790 | -0.45050 | 4.45490 |
| H | 2.12380 | -1.40300 | 5.65880 |

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Compound **5.8**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -465.685497313 hartree.
Free Energy: -465.476518 hartree.

| | | | |
|---|---|---|---|
| H | 1.68258 | 0.93618 | 6.33655 |
| C | 1.26077 | 0.02846 | 6.78195 |
| C | 1.72101 | -1.18280 | 5.92460 |
| H | 1.69467 | -0.05661 | 7.78604 |
| C | 0.83644 | -2.32430 | 6.29098 |
| C | -0.19322 | -2.72665 | 5.54095 |
| C | -1.36653 | -3.45372 | 6.08530 |
| C | -1.72781 | -3.16034 | 7.53938 |
| C | -2.90268 | -4.03024 | 7.97254 |
| C | -2.06106 | -1.64556 | 7.71352 |
| H | -0.85855 | -3.38828 | 8.17090 |
| H | -2.78459 | -1.59847 | 8.53559 |
| H | -2.60337 | -1.29159 | 6.82577 |
| C | -0.90912 | -0.66963 | 8.05593 |
| H | -1.30562 | 0.04171 | 8.78905 |
| C | -0.26906 | 0.16246 | 6.90805 |
| H | -0.12943 | -1.22084 | 8.59580 |
| H | -0.50167 | 1.21897 | 7.07846 |
| H | -0.73471 | -0.09649 | 5.94899 |
| O | -2.08907 | -4.12087 | 5.36708 |

| | | | |
|---|---|---|---|
| H | -2.69631 | -5.09046 | 7.80174 |
| H | -3.80220 | -3.77421 | 7.40376 |
| H | -3.11366 | -3.88324 | 9.03622 |
| H | -0.27934 | -2.40926 | 4.50204 |
| H | 0.93144 | -2.69168 | 7.31220 |
| H | 1.60013 | -0.94594 | 4.86168 |
| H | 2.78086 | -1.38419 | 6.11333 |

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Compound **5.8**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -465.904049460 hartree.
Free Energy: -465.697776 hartree.

| | | | |
|---|---|---|---|
| H | 1.68695 | 0.92763 | 6.31168 |
| C | 1.26732 | 0.02428 | 6.77197 |
| C | 1.74011 | -1.20119 | 5.92413 |
| H | 1.70933 | -0.04357 | 7.77475 |
| C | 0.84913 | -2.33995 | 6.28387 |
| C | -0.17547 | -2.75847 | 5.52500 |
| C | -1.37933 | -3.43563 | 6.05611 |
| C | -1.73373 | -3.16017 | 7.52304 |
| C | -2.89515 | -4.05162 | 7.97442 |
| C | -2.07756 | -1.64206 | 7.73555 |
| H | -0.85705 | -3.38882 | 8.14430 |
| H | -2.77193 | -1.61953 | 8.58474 |
| H | -2.65845 | -1.27853 | 6.87647 |
| C | -0.93324 | -0.64258 | 8.06534 |
| H | -1.35906 | 0.08614 | 8.76682 |
| C | -0.26741 | 0.17494 | 6.90997 |
| H | -0.16295 | -1.16700 | 8.64494 |
| H | -0.47453 | 1.23762 | 7.08649 |
| H | -0.74628 | -0.06231 | 5.95187 |
| O | -2.13971 | -4.04991 | 5.31466 |
| H | -2.67689 | -5.11044 | 7.79860 |
| H | -3.81415 | -3.81232 | 7.42854 |
| H | -3.08671 | -3.91492 | 9.04495 |
| H | -0.23519 | -2.47160 | 4.47499 |
| H | 0.92719 | -2.68903 | 7.31198 |
| H | 1.64648 | -0.96973 | 4.85656 |
| H | 2.79820 | -1.39884 | 6.13670 |

---

Compound **5.8**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -465.890341214 hartree.
Free Energy: -465.683818 hartree.

| | | | |
|---|---|---|---|
| H | 1.68731 | 0.93423 | 6.31607 |
| C | 1.26880 | 0.02788 | 6.77131 |
| C | 1.73857 | -1.19531 | 5.91925 |
| H | 1.71235 | -0.04299 | 7.77345 |
| C | 0.85079 | -2.33862 | 6.27831 |
| C | -0.17619 | -2.75798 | 5.52580 |
| C | -1.37624 | -3.44429 | 6.06248 |
| C | -1.73355 | -3.16193 | 7.53061 |
| C | -2.90346 | -4.04926 | 7.96953 |
| C | -2.07269 | -1.64372 | 7.74172 |
| H | -0.86141 | -3.39608 | 8.15791 |
| H | -2.76842 | -1.61724 | 8.58954 |
| H | -2.65178 | -1.28123 | 6.88121 |
| C | -0.92744 | -0.64385 | 8.06980 |
| H | -1.34901 | 0.08396 | 8.77444 |
| C | -0.26655 | 0.17464 | 6.91181 |
| H | -0.15432 | -1.16760 | 8.64662 |
| H | -0.47810 | 1.23676 | 7.08509 |
| H | -0.74575 | -0.06837 | 5.95558 |
| O | -2.13062 | -4.06701 | 5.32850 |
| H | -2.68163 | -5.10763 | 7.80207 |
| H | -3.80594 | -3.81442 | 7.39651 |
| H | -3.11756 | -3.90225 | 9.03405 |
| H | -0.24319 | -2.47699 | 4.47500 |
| H | 0.92838 | -2.68498 | 7.30761 |
| H | 1.63838 | -0.96221 | 4.85249 |
| H | 2.79915 | -1.39111 | 6.12163 |

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Compound **5.8**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -465.680080100 hartree.
Free Energy: -465.471966 hartree.

| | | | |
|---|---|---|---|
| H | 2.05361 | 0.55391 | 7.02653 |
| C | 1.38589 | -0.31317 | 6.97150 |
| C | 1.62187 | -0.99764 | 5.61194 |
| H | 1.69824 | -0.98081 | 7.78389 |
| C | 0.59371 | -2.06847 | 5.35975 |
| C | 0.16724 | -2.88916 | 6.32126 |
| C | -1.18498 | -3.48698 | 6.22073 |
| C | -2.07813 | -3.07172 | 7.38730 |
| C | -3.46619 | -3.68446 | 7.24996 |
| C | -2.14751 | -1.51798 | 7.44427 |
| H | -1.60366 | -3.42472 | 8.31465 |
| H | -3.06695 | -1.27924 | 7.99066 |
| H | -2.30390 | -1.14288 | 6.42338 |
| C | -0.97304 | -0.75251 | 8.11506 |
| H | -1.41645 | -0.10262 | 8.87687 |
| C | -0.07406 | 0.14430 | 7.21508 |
| H | -0.34515 | -1.45427 | 8.67698 |
| H | -0.03113 | 1.13396 | 7.68162 |
| H | -0.56849 | 0.29873 | 6.24680 |
| O | -1.59915 | -4.09437 | 5.25353 |
| H | -3.41163 | -4.77208 | 7.15113 |
| H | -3.97149 | -3.29739 | 6.35930 |
| H | -4.07903 | -3.44515 | 8.12429 |
| H | 0.61998 | -2.86493 | 7.30968 |
| H | 0.06936 | -2.07524 | 4.40439 |
| H | 1.55302 | -0.24879 | 4.81534 |
| H | 2.64073 | -1.40429 | 5.56692 |
| H | -1.59469 | -3.44565 | 8.28735 |
| H | -3.06677 | -1.32058 | 8.09217 |
| H | -2.40157 | -1.10745 | 6.49217 |
| C | -0.99019 | -0.72481 | 8.12638 |
| H | -1.44116 | -0.04278 | 8.85726 |
| C | -0.07550 | 0.15099 | 7.20630 |
| H | -0.37026 | -1.40183 | 8.72793 |
| H | -0.02330 | 1.14511 | 7.66572 |
| H | -0.57306 | 0.30655 | 6.23997 |
| O | -1.62796 | -4.05557 | 5.19849 |
| H | -3.40612 | -4.79253 | 7.14486 |
| H | -4.00051 | -3.32548 | 6.37223 |
| H | -4.07607 | -3.48121 | 8.14127 |
| H | 0.57770 | -2.84566 | 7.29822 |
| H | 0.17094 | -2.12990 | 4.35443 |
| H | 1.60525 | -0.27377 | 4.80425 |
| H | 2.68474 | -1.40647 | 5.59356 |

---

Compound **5.8**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -465.884852890 hartree.
Free Energy: -465.679071 hartree.

| | | | |
|---|---|---|---|
| H | 2.05449 | 0.56437 | 7.01174 |
| C | 1.39270 | -0.30974 | 6.96463 |
| C | 1.65680 | -1.01510 | 5.61147 |
| H | 1.71057 | -0.95910 | 7.79059 |
| C | 0.64566 | -2.09944 | 5.33445 |
| C | 0.16124 | -2.89445 | 6.29566 |
| C | -1.19796 | -3.47403 | 6.18014 |
| C | -2.08377 | -3.07611 | 7.37213 |
| C | -3.47436 | -3.70611 | 7.25369 |
| C | -2.17415 | -1.51728 | 7.48573 |

---

Compound **5.8**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -465.898361168 hartree.
Free Energy: -465.692986 hartree.

| | | | |
|---|---|---|---|
| H | 2.03859 | 0.59086 | 6.84612 |
| C | 1.38819 | -0.29321 | 6.84520 |
| C | 1.49549 | -0.93751 | 5.44164 |
| H | 1.81303 | -0.96978 | 7.59780 |
| C | 0.47814 | -2.03198 | 5.24351 |
| C | 0.12928 | -2.87664 | 6.22254 |
| C | -1.22050 | -3.48289 | 6.24797 |
| C | -1.96458 | -3.14635 | 7.54749 |
| C | -3.34707 | -3.80250 | 7.58224 |
| C | -2.06737 | -1.59347 | 7.72623 |
| H | -1.35962 | -3.53463 | 8.38117 |
| H | -2.88979 | -1.43692 | 8.43498 |
| H | -2.41018 | -1.15291 | 6.77994 |
| C | -0.83125 | -0.80370 | 8.26213 |
| H | -1.20742 | -0.16390 | 9.06979 |
| C | -0.04394 | 0.13093 | 7.28486 |
| H | -0.13442 | -1.49303 | 8.75540 |
| H | 0.05527 | 1.10073 | 7.78707 |
| H | -0.65699 | 0.32862 | 6.39532 |

| | | | |
|---|---|---|---|
| O | -1.74963 | -4.05096 | 5.30325 |
| H | -3.27728 | -4.88396 | 7.42618 |
| H | -3.99611 | -3.39969 | 6.79689 |
| H | -3.83123 | -3.62600 | 8.54944 |
| H | 0.66093 | -2.85533 | 7.16977 |
| H | -0.10958 | -2.02951 | 4.32584 |
| H | 1.33321 | -0.16768 | 4.67703 |
| H | 2.51964 | -1.30730 | 5.28359 |

---

Compound **5.9**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +56.729229 kJ.

| | | | |
|---|---|---|---|
| H | 0.17030 | -2.74910 | -0.68700 |
| C | -0.13390 | -2.49870 | 0.33020 |
| C | -1.67590 | -2.52690 | 0.39230 |
| H | 0.25920 | -3.30150 | 0.95560 |
| C | -2.25220 | -2.43280 | 1.80230 |
| C | -2.52880 | -1.34440 | 2.55910 |
| C | -2.28420 | 0.07140 | 2.21520 |
| O | -1.97530 | 0.26370 | 0.92990 |
| C | -0.82730 | 1.01680 | 0.58600 |
| H | -0.34550 | 1.41950 | 1.47930 |
| C | -1.25550 | 2.18670 | -0.30750 |
| C | 0.15820 | 0.05910 | -0.11720 |
| H | -0.24530 | -0.26270 | -1.07800 |
| C | 0.55530 | -1.17320 | 0.73040 |
| H | 1.06070 | 0.62410 | -0.35320 |
| H | 0.40970 | -0.97240 | 1.79220 |
| H | 1.63000 | -1.32370 | 0.62130 |
| O | -2.27030 | 0.96740 | 3.05720 |
| H | -2.45110 | -3.39360 | 2.25390 |
| H | -2.11330 | -1.78560 | -0.27430 |
| H | -2.01820 | -3.47850 | -0.01630 |
| H | -1.95320 | 2.83850 | 0.21920 |
| H | -1.74830 | 1.83390 | -1.21380 |
| H | -0.39720 | 2.79000 | -0.60280 |
| H | -2.92320 | -1.50860 | 3.55060 |

---

Compound **5.9**
This structure was assigned as ambiguous.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +72.456444 kJ.

| | | | |
|---|---|---|---|
| H | -1.37550 | -2.14140 | -0.44490 |
| C | -0.48630 | -2.34920 | 0.15250 |
| C | -0.83510 | -2.49470 | 1.64910 |
| H | -0.12580 | -3.31570 | -0.20270 |
| C | -2.32720 | -2.42500 | 1.95980 |
| C | -3.03910 | -1.30410 | 2.21280 |
| C | -2.47040 | 0.04070 | 2.04610 |
| O | -1.89480 | 0.16220 | 0.84140 |
| C | -0.68350 | 0.87150 | 0.66770 |
| H | -0.09290 | 0.84360 | 1.58540 |
| C | -0.99050 | 2.33080 | 0.29900 |
| C | 0.08570 | 0.14160 | -0.45450 |
| H | -0.53550 | 0.10070 | -1.35040 |
| C | 0.59930 | -1.28120 | -0.12440 |
| H | 0.95000 | 0.74880 | -0.72590 |
| H | 1.31690 | -1.24220 | 0.69600 |
| H | 1.17590 | -1.61630 | -0.98750 |
| O | -2.44800 | 0.89670 | 2.92830 |
| H | -2.82650 | -3.37860 | 2.04770 |
| H | -0.45160 | -3.44240 | 2.02950 |
| H | -0.32350 | -1.73240 | 2.23800 |
| H | -1.54390 | 2.82750 | 1.09650 |
| H | -1.58970 | 2.39240 | -0.60970 |
| H | -0.07280 | 2.89580 | 0.13650 |
| H | -4.07410 | -1.36690 | 2.51220 |

---

Compound **5.9**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -501.617840620 hartree.
Free Energy: -501.431647 hartree.

| | | | |
|---|---|---|---|
| H | 0.17527 | -2.67821 | -0.64541 |
| C | -0.16043 | -2.43893 | 0.37179 |
| C | -1.70415 | -2.47722 | 0.36085 |
| H | 0.20783 | -3.24661 | 1.01645 |
| C | -2.33102 | -2.44158 | 1.73265 |
| C | -2.53648 | -1.39664 | 2.54738 |

| | | | |
|---|---|---|---|
| C | -2.05848 | -0.02022 | 2.28816 |
| O | -1.93141 | 0.24791 | 0.97431 |
| C | -0.81108 | 1.05459 | 0.55556 |
| H | -0.37555 | 1.51245 | 1.44918 |
| C | -1.31736 | 2.12483 | -0.38903 |
| C | 0.18896 | 0.09388 | -0.08511 |
| H | -0.21202 | -0.23915 | -1.05291 |
| C | 0.51209 | -1.12749 | 0.79975 |
| H | 1.10017 | 0.66233 | -0.30368 |
| H | 0.27338 | -0.90639 | 1.84904 |
| H | 1.59278 | -1.30673 | 0.78194 |
| O | -1.77295 | 0.76232 | 3.16595 |
| H | -2.62769 | -3.41279 | 2.12864 |
| H | -2.08523 | -1.66328 | -0.25803 |
| H | -2.00356 | -3.41646 | -0.11548 |
| H | -2.01242 | 2.79565 | 0.12342 |
| H | -1.83425 | 1.66902 | -1.23990 |
| H | -0.47978 | 2.71731 | -0.76991 |
| H | -2.95190 | -1.54919 | 3.53900 |

---

Compound **5.9**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -501.841339151 hartree.
Free Energy: -501.657571 hartree.

| | | | |
|---|---|---|---|
| H | 0.13853 | -2.69963 | -0.67333 |
| C | -0.15988 | -2.45464 | 0.35548 |
| C | -1.71135 | -2.51291 | 0.39119 |
| H | 0.23690 | -3.26189 | 0.98599 |
| C | -2.33364 | -2.45247 | 1.76622 |
| C | -2.56824 | -1.38517 | 2.55330 |
| C | -2.12126 | -0.00411 | 2.27981 |
| O | -1.93593 | 0.23314 | 0.95772 |
| C | -0.80583 | 1.05672 | 0.55361 |
| H | -0.38520 | 1.50315 | 1.45969 |
| C | -1.30814 | 2.14896 | -0.37656 |
| C | 0.21406 | 0.10781 | -0.09050 |
| H | -0.15259 | -0.19812 | -1.08042 |
| C | 0.54549 | -1.14356 | 0.76046 |
| H | 1.12728 | 0.69018 | -0.26863 |
| H | 0.36828 | -0.93196 | 1.82323 |
| H | 1.62244 | -1.34069 | 0.68373 |
| O | -1.90428 | 0.81694 | 3.15318 |
| H | -2.61355 | -3.41858 | 2.18778 |
| H | -2.11602 | -1.72089 | -0.24153 |
| H | -2.00344 | -3.46861 | -0.06063 |
| H | -2.01189 | 2.80776 | 0.14307 |
| H | -1.81537 | 1.71876 | -1.24782 |
| H | -0.46948 | 2.75728 | -0.73417 |
| H | -2.99218 | -1.52808 | 3.54371 |

---

Compound **5.9**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -501.828584718 hartree.
Free Energy: -501.644604 hartree.

| | | | |
|---|---|---|---|
| H | 0.13804 | -2.69347 | -0.67536 |
| C | -0.16265 | -2.45208 | 0.35396 |
| C | -1.71412 | -2.50955 | 0.38983 |
| H | 0.23398 | -3.26174 | 0.98153 |
| C | -2.33654 | -2.45230 | 1.76649 |
| C | -2.56662 | -1.38561 | 2.55362 |
| C | -2.11065 | -0.00539 | 2.28073 |
| O | -1.93130 | 0.22895 | 0.95282 |
| C | -0.80860 | 1.05604 | 0.55343 |
| H | -0.39415 | 1.50538 | 1.46124 |
| C | -1.31317 | 2.14607 | -0.38056 |
| C | 0.21818 | 0.11016 | -0.08714 |
| H | -0.14390 | -0.19629 | -1.07877 |
| C | 0.54319 | -1.14269 | 0.76537 |
| H | 1.13342 | 0.69060 | -0.26252 |
| H | 0.35726 | -0.93160 | 1.82625 |
| H | 1.62028 | -1.34138 | 0.69646 |
| O | -1.86938 | 0.80706 | 3.15082 |
| H | -2.61833 | -3.41900 | 2.18590 |
| H | -2.11957 | -1.71378 | -0.23715 |
| H | -2.00715 | -3.46285 | -0.06734 |
| H | -2.02571 | 2.79579 | 0.13666 |
| H | -1.81215 | 1.70921 | -1.25286 |
| H | -0.47792 | 2.76109 | -0.73439 |
| H | -2.98776 | -1.52322 | 3.54557 |

---

Compound **5.9**
This structure was assigned as ambiguous.

M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -501.615894007 hartree.
Free Energy: -501.429785 hartree.

| | | | |
|---|---|---|---|
| H | 0.55769 | -2.85883 | 1.39070 |
| C | -0.07878 | -2.02074 | 1.08530 |
| C | -1.46151 | -2.57521 | 0.65586 |
| H | -0.18225 | -1.40249 | 1.98417 |
| C | -2.52903 | -2.46662 | 1.72422 |
| C | -2.88493 | -1.36045 | 2.39246 |
| C | -2.20832 | -0.05612 | 2.18236 |
| O | -1.88161 | 0.11103 | 0.89176 |
| C | -0.71160 | 0.88733 | 0.55412 |
| H | -0.09464 | 0.97940 | 1.45636 |
| C | -1.13874 | 2.26168 | 0.07597 |
| C | -0.00979 | 0.05262 | -0.51247 |
| H | -0.76475 | -0.19813 | -1.26850 |
| C | 0.67804 | -1.21921 | 0.01574 |
| H | 0.73844 | 0.67481 | -1.01752 |
| H | 1.64629 | -0.93677 | 0.44774 |
| H | 0.90328 | -1.87095 | -0.83764 |
| O | -1.94330 | 0.73682 | 3.05731 |
| H | -3.03679 | -3.39015 | 1.99842 |
| H | -1.80940 | -2.04306 | -0.23595 |
| H | -1.36024 | -3.62608 | 0.37073 |
| H | -1.70132 | 2.77624 | 0.85989 |
| H | -1.77133 | 2.17680 | -0.81376 |
| H | -0.26217 | 2.86581 | -0.17702 |
| H | -3.60794 | -1.39912 | 3.20123 |

---

Compound **5.9**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -501.837745509 hartree.
Free Energy: -501.654338 hartree.

| | | | |
|---|---|---|---|
| H | 0.56812 | -2.93049 | 1.31274 |
| C | -0.06878 | -2.07141 | 1.06595 |
| C | -1.47793 | -2.60060 | 0.65493 |
| H | -0.14550 | -1.50189 | 1.99793 |
| C | -2.53371 | -2.47097 | 1.73603 |
| C | -2.88528 | -1.35617 | 2.40362 |
| C | -2.22291 | -0.04537 | 2.20448 |
| O | -1.88263 | 0.12770 | 0.90931 |
| C | -0.71081 | 0.92001 | 0.55695 |
| H | -0.10502 | 1.04321 | 1.46134 |
| C | -1.15233 | 2.28442 | 0.04577 |
| C | 0.01069 | 0.06989 | -0.49310 |
| H | -0.72413 | -0.16914 | -1.27302 |
| C | 0.68734 | -1.22124 | 0.02349 |
| H | 0.77690 | 0.68879 | -0.97798 |
| H | 1.65260 | -0.95294 | 0.47480 |
| H | 0.92894 | -1.84361 | -0.84910 |
| O | -1.98383 | 0.75466 | 3.09106 |
| H | -3.03870 | -3.39221 | 2.02617 |
| H | -1.82621 | -2.06698 | -0.23599 |
| H | -1.40237 | -3.65550 | 0.37058 |
| H | -1.71614 | 2.81830 | 0.81722 |
| H | -1.78625 | 2.18325 | -0.84283 |
| H | -0.27905 | 2.89049 | -0.22175 |
| H | -3.59769 | -1.40357 | 3.22289 |

---

Compound **5.9**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -501.825093737 hartree.
Free Energy: -501.641184 hartree.

| | | | |
|---|---|---|---|
| H | 0.56751 | -2.93251 | 1.30927 |
| C | -0.06823 | -2.07292 | 1.06103 |
| C | -1.48062 | -2.59860 | 0.65487 |
| H | -0.14410 | -1.50140 | 1.99124 |
| C | -2.52897 | -2.46825 | 1.74484 |
| C | -2.88487 | -1.35114 | 2.40449 |
| C | -2.23668 | -0.03416 | 2.19176 |
| O | -1.87315 | 0.11205 | 0.89491 |
| C | -0.70935 | 0.91241 | 0.55695 |
| H | -0.10915 | 1.03234 | 1.46620 |
| C | -1.15563 | 2.28080 | 0.05695 |
| C | 0.02088 | 0.07173 | -0.49563 |
| H | -0.71022 | -0.16044 | -1.28099 |
| C | 0.69034 | -1.22615 | 0.01647 |
| H | 0.79146 | 0.69160 | -0.97254 |

| | | | |
|---|---|---|---|
| H | 1.65867 | -0.96536 | 0.46556 |
| H | 0.92709 | -1.84869 | -0.85727 |
| O | -2.01628 | 0.78475 | 3.06117 |
| H | -3.02256 | -3.39153 | 2.04768 |
| H | -1.83340 | -2.06074 | -0.23110 |
| H | -1.40805 | -3.65315 | 0.36693 |
| H | -1.71945 | 2.79930 | 0.83759 |
| H | -1.79280 | 2.18058 | -0.82898 |
| H | -0.28688 | 2.89367 | -0.20916 |
| H | -3.59024 | -1.39558 | 3.22927 |

---

Compound **5.10**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +72.767899 kJ.

| | | | |
|---|---|---|---|
| H | -0.25030 | 0.97760 | 14.98740 |
| C | -1.04660 | 0.32280 | 14.63130 |
| C | -0.67290 | -0.15990 | 13.21260 |
| H | -1.04040 | -0.53290 | 15.30780 |
| C | -1.54960 | -1.29580 | 12.67680 |
| C | -2.73310 | -1.18540 | 12.02030 |
| C | -3.50020 | 0.04100 | 11.70900 |
| O | -2.82000 | 1.17200 | 11.90710 |
| C | -3.39040 | 2.21060 | 12.68140 |
| H | -4.40890 | 1.95650 | 12.98200 |
| C | -3.43510 | 3.48830 | 11.83530 |
| C | -2.52540 | 2.36530 | 13.95010 |
| H | -1.53660 | 2.74610 | 13.69150 |
| C | -2.39200 | 1.06980 | 14.78570 |
| H | -2.98220 | 3.13540 | 14.57280 |
| H | -3.22790 | 0.39740 | 14.59050 |
| H | -2.49140 | 1.33790 | 15.83820 |
| O | -4.68780 | 0.01610 | 11.38970 |
| C | -0.97570 | -2.67290 | 12.96540 |
| H | -0.60710 | 0.67200 | 12.51460 |
| H | 0.35300 | -0.52900 | 13.24450 |
| H | -4.05010 | 3.34080 | 10.94700 |
| H | -2.43800 | 3.78100 | 11.50560 |
| H | -3.86140 | 4.31790 | 12.39920 |
| H | -3.23050 | -2.09580 | 11.72190 |
| H | -1.62620 | -3.47110 | 12.60600 |
| H | -0.84150 | -2.80940 | 14.03880 |
| H | -0.00570 | -2.79050 | 12.48150 |

---

Compound **5.10**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +87.679649 kJ.

| | | | |
|---|---|---|---|
| H | -0.37520 | 0.57120 | 12.93770 |
| C | -0.73820 | 0.50650 | 13.96460 |
| C | -1.63330 | -0.73950 | 14.16630 |
| H | 0.16130 | 0.35720 | 14.56360 |
| C | -1.86230 | -1.54120 | 12.88200 |
| C | -2.51010 | -1.09940 | 11.77580 |
| C | -3.15630 | 0.21750 | 11.62050 |
| O | -3.67210 | 0.68110 | 12.77770 |
| C | -3.65620 | 2.05440 | 13.15260 |
| H | -4.10740 | 2.07420 | 14.14490 |
| C | -4.54490 | 2.94550 | 12.26630 |
| C | -2.21080 | 2.57690 | 13.31230 |
| H | -1.68780 | 2.57000 | 12.35500 |
| C | -1.36820 | 1.85350 | 14.38920 |
| H | -2.27330 | 3.62820 | 13.59560 |
| H | -1.93790 | 1.74020 | 15.31230 |
| H | -0.54430 | 2.52190 | 14.64280 |
| O | -3.14870 | 0.83700 | 10.55840 |
| C | -1.22770 | -2.92040 | 12.89890 |
| H | -1.15950 | -1.39030 | 14.90270 |
| H | -2.58870 | -0.48420 | 14.62410 |
| H | -5.54650 | 2.52560 | 12.17310 |
| H | -4.13760 | 3.06580 | 11.26270 |
| H | -4.64420 | 3.94220 | 12.69570 |
| H | -2.54970 | -1.73320 | 10.90310 |
| H | -1.40510 | -3.46090 | 11.96860 |
| H | -1.63650 | -3.51610 | 13.71570 |
| H | -0.14950 | -2.83810 | 13.03990 |

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Compound **5.10**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in methanol was used.

Electronic Energy: -540.918232296 hartree.

Free Energy: -540.705854 hartree.

| | | | |
|---|---|---|---|
| H | -0.36549 | 0.96932 | 14.99957 |
| C | -1.15638 | 0.31496 | 14.61164 |
| C | -0.71733 | -0.13451 | 13.20161 |
| H | -1.17710 | -0.56393 | 15.26894 |
| C | -1.52189 | -1.29515 | 12.65521 |
| C | -2.74658 | -1.23288 | 12.09726 |
| C | -3.58076 | -0.02577 | 12.00871 |
| O | -2.87944 | 1.11802 | 11.96973 |
| C | -3.39701 | 2.27147 | 12.67527 |
| H | -4.44978 | 2.08034 | 12.90314 |
| C | -3.26217 | 3.47461 | 11.76633 |
| C | -2.58572 | 2.38198 | 13.96421 |
| H | -1.57681 | 2.73979 | 13.71533 |
| C | -2.49331 | 1.05770 | 14.74757 |
| H | -3.05231 | 3.16105 | 14.57763 |
| H | -3.32758 | 0.39614 | 14.47616 |
| H | -2.62857 | 1.26416 | 15.81493 |
| O | -4.79929 | -0.05883 | 11.99507 |
| C | -0.86789 | -2.63538 | 12.83700 |
| H | -0.73358 | 0.71504 | 12.51722 |
| H | 0.32335 | -0.46891 | 13.27903 |
| H | -3.86095 | 3.34578 | 10.86011 |
| H | -2.21536 | 3.61859 | 11.47870 |
| H | -3.60557 | 4.37477 | 12.28516 |
| H | -3.25666 | -2.14759 | 11.80745 |
| H | -1.50519 | -3.46070 | 12.51092 |
| H | -0.60902 | -2.78285 | 13.89328 |
| H | 0.07436 | -2.67140 | 12.27682 |

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Compound **5.10**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in methanol was used.

Electronic Energy: -541.162058754 hartree.
Free Energy: -540.952895 hartree.

| | | | |
|---|---|---|---|
| H | -0.31591 | 0.99693 | 14.96269 |
| C | -1.12231 | 0.33530 | 14.61753 |
| C | -0.69805 | -0.17409 | 13.21331 |
| H | -1.12912 | -0.51695 | 15.31074 |
| C | -1.51920 | -1.32499 | 12.66001 |
| C | -2.73310 | -1.23254 | 12.06669 |
| C | -3.55450 | -0.02352 | 11.94560 |
| O | -2.84684 | 1.12712 | 11.97482 |
| C | -3.40059 | 2.27969 | 12.68201 |
| H | -4.44821 | 2.05535 | 12.90224 |
| C | -3.30707 | 3.49061 | 11.76935 |
| C | -2.59968 | 2.41044 | 13.98305 |
| H | -1.60577 | 2.81960 | 13.75468 |
| C | -2.45797 | 1.08962 | 14.77785 |
| H | -3.10945 | 3.16383 | 14.59702 |
| H | -3.30144 | 0.42291 | 14.55378 |
| H | -2.55110 | 1.31679 | 15.84758 |
| O | -4.77757 | -0.05219 | 11.84372 |
| C | -0.89703 | -2.68366 | 12.84041 |
| H | -0.68714 | 0.65969 | 12.50955 |
| H | 0.33637 | -0.52642 | 13.30788 |
| H | -3.90655 | 3.34414 | 10.86425 |
| H | -2.26825 | 3.67805 | 11.47345 |
| H | -3.68138 | 4.38046 | 12.28809 |
| H | -3.24579 | -2.14044 | 11.75854 |
| H | -1.54196 | -3.49345 | 12.48641 |
| H | -0.66423 | -2.85923 | 13.89991 |
| H | 0.05984 | -2.73727 | 12.30284 |

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Compound **5.10**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -541.148456149 hartree.
Free Energy: -540.938224 hartree.

| | | | |
|---|---|---|---|
| H | -0.31465 | 1.00157 | 14.96340 |
| C | -1.11887 | 0.33748 | 14.61644 |
| C | -0.69945 | -0.17196 | 13.21107 |
| H | -1.12434 | -0.51343 | 15.31190 |
| C | -1.52120 | -1.32572 | 12.65915 |
| C | -2.72892 | -1.22977 | 12.06283 |
| C | -3.56024 | -0.01680 | 11.94684 |
| O | -2.83210 | 1.13437 | 11.97570 |
| C | -3.39399 | 2.27251 | 12.67500 |
| H | -4.44178 | 2.04035 | 12.88942 |
| C | -3.30893 | 3.49182 | 11.76863 |
| C | -2.60111 | 2.41105 | 13.98331 |
| H | -1.60641 | 2.82236 | 13.76005 |
| C | -2.45788 | 1.08805 | 14.77621 |
| H | -3.11097 | 3.16315 | 14.59958 |

| | | | |
|---|---|---|---|
| H | -3.29644 | 0.41971 | 14.54292 |
| H | -2.55719 | 1.31057 | 15.84640 |
| O | -4.77351 | -0.04157 | 11.87553 |
| C | -0.89834 | -2.68763 | 12.84446 |
| H | -0.69950 | 0.65997 | 12.50600 |
| H | 0.33861 | -0.51778 | 13.30049 |
| H | -3.90423 | 3.33968 | 10.86318 |
| H | -2.27126 | 3.68395 | 11.47329 |
| H | -3.68874 | 4.37951 | 12.28722 |
| H | -3.24548 | -2.13399 | 11.75177 |
| H | -1.54252 | -3.49480 | 12.48435 |
| H | -0.67638 | -2.87010 | 13.90508 |
| H | 0.06184 | -2.74674 | 12.31377 |

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Compound **5.10**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
SMD implicit solvation in methanol was used.

Electronic Energy: -541.158834266 hartree.
Free Energy: -540.950351 hartree.

| | | | |
|---|---|---|---|
| H | -0.86137 | 0.08482 | 15.44469 |
| C | -1.51923 | 0.28069 | 14.58978 |
| C | -0.76997 | -0.22059 | 13.30836 |
| H | -2.41289 | -0.33291 | 14.76025 |
| C | -1.46357 | -1.34775 | 12.55712 |
| C | -2.65855 | -1.25228 | 11.92956 |
| C | -3.51412 | -0.06030 | 11.91304 |
| O | -2.81054 | 1.08658 | 11.98482 |
| C | -3.42582 | 2.27480 | 12.56432 |
| H | -4.48016 | 2.28981 | 12.27455 |
| C | -2.71090 | 3.46961 | 11.95302 |
| C | -3.30726 | 2.15925 | 14.08940 |
| H | -3.61307 | 3.12689 | 14.50906 |
| C | -1.92134 | 1.77584 | 14.65322 |
| H | -4.04524 | 1.42569 | 14.44174 |
| H | -1.93633 | 2.05568 | 15.71458 |
| H | -1.13532 | 2.39265 | 14.19748 |
| O | -4.73923 | -0.09896 | 11.84330 |
| C | -0.75422 | -2.67389 | 12.59372 |
| H | -0.59658 | 0.61790 | 12.62964 |
| H | 0.21918 | -0.58484 | 13.60526 |
| H | -2.80992 | 3.45968 | 10.86200 |
| H | -1.64434 | 3.47598 | 12.20212 |
| H | -3.15630 | 4.39769 | 12.32770 |
| H | -3.11712 | -2.13946 | 11.50025 |
| H | -1.30259 | -3.46051 | 12.06651 |
| H | -0.59482 | -2.99294 | 13.63321 |
| H | 0.24482 | -2.58313 | 12.14490 |

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Compound **5.10**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -541.145332066 hartree.
Free Energy: -540.935840 hartree.

| | | | |
|---|---|---|---|
| H | -0.87060 | 0.08063 | 15.45345 |
| C | -1.52058 | 0.27951 | 14.59284 |
| C | -0.77111 | -0.22448 | 13.31289 |
| H | -2.41777 | -0.33001 | 14.75731 |
| C | -1.46554 | -1.35249 | 12.55964 |
| C | -2.65375 | -1.24975 | 11.92862 |
| C | -3.51473 | -0.05197 | 11.91102 |
| O | -2.78801 | 1.09397 | 11.99471 |
| C | -3.41891 | 2.26662 | 12.56135 |
| H | -4.47408 | 2.25865 | 12.27300 |
| C | -2.72403 | 3.47690 | 11.95055 |
| C | -3.30325 | 2.16316 | 14.09015 |
| H | -3.60668 | 3.13098 | 14.51209 |
| C | -1.91634 | 1.77776 | 14.65312 |
| H | -4.04129 | 1.43126 | 14.44447 |
| H | -1.92256 | 2.06486 | 15.71259 |
| H | -1.12919 | 2.38763 | 14.18960 |
| O | -4.72857 | -0.08110 | 11.84894 |
| C | -0.75432 | -2.68153 | 12.59382 |
| H | -0.60430 | 0.61295 | 12.63227 |
| H | 0.21995 | -0.58522 | 13.61148 |
| H | -2.81624 | 3.45734 | 10.86013 |
| H | -1.65824 | 3.49985 | 12.20135 |
| H | -3.18401 | 4.40028 | 12.31918 |
| H | -3.11459 | -2.13144 | 11.49155 |
| H | -1.30110 | -3.46190 | 12.05670 |
| H | -0.60398 | -3.01387 | 13.63040 |
| H | 0.24704 | -2.59260 | 12.15039 |

---

Compound **5.10**
This structure was assigned as ambiguous.

M06-2X/6-31g(d)
SMD implicit solvation in methanol was used.

Electronic Energy: -540.916732539 hartree.
Free Energy: -540.703686 hartree.

| | | | |
|---|---|---|---|
| H | -1.84099 | -0.40618 | 15.53155 |
| C | -1.99050 | 0.14844 | 14.59823 |
| C | -0.95478 | -0.34694 | 13.55751 |
| H | -3.00577 | -0.10953 | 14.27647 |
| C | -1.49437 | -1.38408 | 12.58555 |
| C | -2.59706 | -1.22285 | 11.82860 |
| C | -3.44036 | -0.01469 | 11.88021 |
| O | -2.71634 | 1.09218 | 12.07426 |
| C | -3.28676 | 2.20937 | 12.80015 |
| H | -4.16917 | 1.84583 | 13.33999 |
| C | -3.68194 | 3.29107 | 11.81461 |
| C | -2.18035 | 2.62314 | 13.76306 |
| H | -1.26820 | 2.74919 | 13.16575 |
| C | -1.94045 | 1.64731 | 14.92829 |
| H | -2.42159 | 3.61067 | 14.17314 |
| H | -2.69854 | 1.83300 | 15.69925 |
| H | -0.97301 | 1.88846 | 15.38593 |
| O | -4.65539 | -0.01086 | 11.78347 |
| C | -0.73459 | -2.67720 | 12.53658 |
| H | -0.56587 | 0.50070 | 12.98391 |
| H | -0.09706 | -0.78365 | 14.07903 |
| H | -4.41834 | 2.90563 | 11.10290 |
| H | -2.80426 | 3.63996 | 11.26005 |
| H | -4.12125 | 4.14196 | 12.34364 |
| H | -2.98226 | -2.04091 | 11.22642 |
| H | -1.16549 | -3.38804 | 11.82714 |
| H | -0.71017 | -3.13752 | 13.53196 |
| H | 0.30868 | -2.48527 | 12.25602 |

---

Compound **5.11**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +213.728119 kJ.

| | | | |
|---|---|---|---|
| H | -3.70930 | 3.78020 | -9.41970 |
| C | -3.76700 | 2.94080 | -10.10660 |
| C | -4.91760 | 2.49220 | -12.38000 |
| C | -2.40550 | 2.92420 | -12.21860 |
| C | -3.62750 | 2.94070 | -13.10670 |
| C | -2.45010 | 2.91720 | -10.87720 |
| C | -5.02800 | 3.14710 | -10.96980 |
| H | -4.81640 | 1.42050 | -12.19800 |
| H | -3.71690 | 3.95550 | -13.49120 |
| H | -5.19110 | 4.21560 | -11.10630 |
| H | -3.43250 | 2.29230 | -13.96060 |
| C | -6.17520 | 2.68180 | -13.28560 |
| H | -7.05890 | 2.41100 | -12.71230 |
| C | -6.17080 | 1.71890 | -14.48510 |
| H | -5.37130 | 1.94840 | -15.18930 |
| H | -7.11160 | 1.77440 | -15.03370 |
| H | -6.04490 | 0.68500 | -14.16220 |
| C | -6.40800 | 4.12830 | -13.76260 |
| H | -6.38590 | 4.84180 | -12.94060 |
| H | -7.38270 | 4.22310 | -14.24210 |
| H | -5.66390 | 4.44290 | -14.49390 |
| C | -4.04740 | 1.64600 | -9.32360 |
| H | -3.59850 | 0.81030 | -9.86270 |
| C | -6.12790 | 2.52700 | -10.06980 |
| H | -6.87390 | 2.00620 | -10.66480 |
| O | -5.46400 | 1.45800 | -9.39960 |
| C | -3.56470 | 1.59510 | -7.83900 |
| H | -3.59890 | 0.55900 | -7.49970 |
| H | -2.52760 | 1.91050 | -7.73510 |
| C | -6.93980 | 3.53240 | -9.15640 |
| C | -7.70180 | 2.91920 | -7.93020 |
| H | -8.59790 | 3.50950 | -7.73530 |
| H | -8.07300 | 1.93170 | -8.20860 |
| C | -4.46570 | 2.41070 | -6.93040 |
| C | -3.94780 | 3.77970 | -6.51250 |
| H | -3.81750 | 4.45810 | -7.35260 |
| H | -2.97460 | 3.66580 | -6.03430 |
| H | -4.59840 | 4.25980 | -5.78270 |
| C | -5.72610 | 1.97300 | -6.75980 |
| C | -6.94480 | 2.83380 | -6.57260 |
| H | -6.70210 | 3.82780 | -6.20030 |
| H | -5.97060 | 0.97960 | -7.11160 |
| H | -7.58360 | 2.37050 | -5.82060 |
| C | -1.18120 | 2.91450 | -10.04610 |
| H | -1.06950 | 1.96650 | -9.52110 |
| H | -1.20380 | 3.72030 | -9.31180 |
| H | -0.29680 | 3.05320 | -10.66870 |
| H | -1.45190 | 2.94070 | -12.72650 |
| C | -7.95990 | 4.27130 | -10.04270 |
| H | -8.69410 | 3.58160 | -10.45970 |
| H | -7.47750 | 4.77900 | -10.87650 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -8.50490 | 5.03230 | -9.48290 | C | -0.98730 | 2.46880 | -10.11500 |
| O | -6.10830 | 4.56050 | -8.67280 | H | -1.01230 | 1.51080 | -9.59600 |
| H | -5.50390 | 4.14310 | -8.07290 | H | -0.81520 | 3.25650 | -9.38120 |
| 54 | | | | H | -0.13620 | 2.45400 | -10.79650 |
| Molecule Name | | | | H | -1.39930 | 2.78690 | -12.76000 |
| H | -3.33860 | 3.70830 | -9.36030 | C | -8.00660 | 2.56360 | -8.37630 |
| C | -3.54370 | 2.85510 | -9.99610 | H | -7.55320 | 1.97380 | -7.58250 |
| C | -4.84780 | 2.68020 | -12.23190 | H | -8.49340 | 1.86040 | -9.05210 |
| C | -2.31590 | 2.84710 | -12.19070 | H | -8.78270 | 3.18040 | -7.92190 |
| C | -3.57170 | 3.12160 | -12.98090 | O | -7.69300 | 4.08840 | -10.10330 |
| C | -2.28920 | 2.71170 | -10.85590 | H | -8.00880 | 3.44390 | -10.71780 |
| C | -4.84550 | 3.18130 | -10.75410 | | | | |
| H | -4.80330 | 1.59070 | -12.17360 | ---------- | | | |
| H | -3.58630 | 4.18710 | -13.20700 | | | | |
| H | -4.98020 | 4.26200 | -10.75960 | Compound **5.11** | | | |
| H | -3.48820 | 2.59330 | -13.93020 | This structure was assigned as correct. | | | |
| C | -6.13870 | 3.03610 | -13.03340 | | | | |
| H | -6.99910 | 2.70280 | -12.45750 | Molecular Mechanics (OPLS-2005), gas | | | |
| C | -6.23070 | 2.26450 | -14.36110 | phase. | | | |
| H | -5.47680 | 2.59200 | -15.07680 | Energy: +193.184494 kJ. | | | |
| H | -7.20430 | 2.41030 | -14.83020 | | | | |
| H | -6.10260 | 1.19260 | -14.20680 | H | -3.70930 | 3.78020 | -9.41970 |
| C | -6.34380 | 4.54390 | -13.27340 | C | -3.76700 | 2.94080 | -10.10660 |
| H | -6.33650 | 5.11170 | -12.34340 | C | -4.91760 | 2.49220 | -12.38000 |
| H | -7.30770 | 4.73130 | -13.74730 | C | -2.40550 | 2.92420 | -12.21860 |
| H | -5.58050 | 4.96390 | -13.92750 | C | -3.62750 | 2.94070 | -13.10670 |
| C | -3.86390 | 1.61100 | -9.14020 | C | -2.45010 | 2.91720 | -10.87720 |
| H | -3.50570 | 0.72150 | -9.66050 | C | -5.02800 | 3.14710 | -10.96980 |
| C | -5.93420 | 2.50790 | -9.88370 | H | -4.81640 | 1.42050 | -12.19800 |
| H | -6.54610 | 1.88050 | -10.52990 | H | -3.71690 | 3.95550 | -13.49120 |
| O | -5.28940 | 1.52210 | -9.08810 | H | -5.19110 | 4.21560 | -11.10630 |
| C | -3.30590 | 1.62590 | -7.68250 | H | -3.43250 | 2.29230 | -13.96060 |
| H | -3.10960 | 0.60760 | -7.34620 | C | -6.17520 | 2.68180 | -13.28560 |
| H | -2.35560 | 2.15680 | -7.62960 | H | -7.05890 | 2.41100 | -12.71230 |
| C | -6.95470 | 3.42110 | -9.10000 | C | -6.17080 | 1.71890 | -14.48510 |
| C | -6.44020 | 4.58280 | -8.18330 | H | -5.37130 | 1.94840 | -15.18930 |
| H | -5.70000 | 5.17340 | -8.72350 | H | -7.11160 | 1.77440 | -15.03370 |
| H | -7.27290 | 5.27000 | -8.02360 | H | -6.04490 | 0.68500 | -14.16220 |
| C | -4.32000 | 2.26530 | -6.75290 | C | -6.40800 | 4.12830 | -13.76260 |
| C | -5.23240 | 1.29340 | -6.01980 | H | -6.38590 | 4.84180 | -12.94060 |
| H | -4.63260 | 0.58470 | -5.44900 | H | -7.38270 | 4.22310 | -14.24210 |
| H | -5.84000 | 0.72220 | -6.72050 | H | -5.66390 | 4.44290 | -14.49390 |
| H | -5.89050 | 1.79510 | -5.31230 | C | -4.04740 | 1.64600 | -9.32360 |
| C | -4.56560 | 3.57550 | -6.91270 | H | -3.59850 | 0.81030 | -9.86270 |
| C | -5.90410 | 4.24400 | -6.76750 | C | -6.12790 | 2.52700 | -10.06980 |
| H | -5.75880 | 5.16400 | -6.20110 | H | -6.87390 | 2.00620 | -10.66480 |
| H | -3.86160 | 4.17840 | -7.45920 | O | -5.46400 | 1.45800 | -9.39960 |
| H | -6.62050 | 3.64730 | -6.20710 | C | -3.56470 | 1.59510 | -7.83900 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.59890 | 0.55900 | -7.49970 | H | 1.01555 | -0.36841 | -1.33290 |
| H | -2.52760 | 1.91050 | -7.73510 | H | 3.98771 | 1.48216 | 0.28169 |
| C | -6.93980 | 3.53240 | -9.15640 | C | 3.14690 | -1.22789 | 0.36877 |
| C | -7.70180 | 2.91920 | -7.93020 | H | 2.48079 | -2.01788 | 0.73960 |
| H | -8.59790 | 3.50950 | -7.73530 | C | 4.31764 | -1.14725 | 1.36392 |
| H | -8.07300 | 1.93170 | -8.20860 | H | 5.06450 | -0.40661 | 1.05379 |
| C | -4.46570 | 2.41070 | -6.93040 | H | 4.83053 | -2.11363 | 1.43940 |
| C | -3.94780 | 3.77970 | -6.51250 | H | 3.97095 | -0.87344 | 2.36762 |
| H | -3.81750 | 4.45810 | -7.35260 | C | 3.65532 | -1.68454 | -1.01059 |
| H | -2.97460 | 3.66580 | -6.03430 | H | 2.86335 | -1.69230 | -1.76772 |
| H | -4.59840 | 4.25980 | -5.78270 | H | 4.05844 | -2.70207 | -0.94647 |
| C | -5.72610 | 1.97300 | -6.75980 | H | 4.46186 | -1.04151 | -1.38136 |
| C | -6.94480 | 2.83380 | -6.57260 | C | -0.66182 | 1.22253 | 1.08869 |
| H | -6.70210 | 3.82780 | -6.20030 | H | -0.09583 | 1.76968 | 1.85594 |
| H | -5.97060 | 0.97960 | -7.11160 | C | -0.02640 | -0.99846 | 0.48942 |
| H | -7.58360 | 2.37050 | -5.82060 | H | 0.53545 | -1.72506 | 1.08699 |
| C | -1.18120 | 2.91450 | -10.04610 | O | -0.66060 | -0.15835 | 1.46696 |
| H | -1.06950 | 1.96650 | -9.52110 | C | -2.12670 | 1.78157 | 1.10590 |
| H | -1.20380 | 3.72030 | -9.31180 | H | -2.43097 | 1.83830 | 2.15839 |
| H | -0.29680 | 3.05320 | -10.66870 | H | -2.12413 | 2.80771 | 0.72140 |
| H | -1.45190 | 2.94070 | -12.72650 | C | -0.97481 | -1.86757 | -0.43013 |
| C | -7.95990 | 4.27130 | -10.04270 | C | -2.22171 | -2.47499 | 0.29874 |
| H | -8.69410 | 3.58160 | -10.45970 | H | -2.42689 | -3.45223 | -0.15626 |
| H | -7.47750 | 4.77900 | -10.87650 | H | -1.96663 | -2.66452 | 1.34907 |
| H | -8.50490 | 5.03230 | -9.48290 | C | -3.06216 | 0.87132 | 0.33855 |
| O | -6.10830 | 4.56050 | -8.67280 | C | -3.55321 | 1.31502 | -1.02123 |
| H | -5.50390 | 4.14310 | -8.07290 | H | -2.74563 | 1.63483 | -1.69515 |
| | | | | H | -4.20858 | 2.19019 | -0.90754 |
| ---------- | | | | H | -4.13744 | 0.54174 | -1.53035 |
| | | | | C | -3.28035 | -0.33388 | 0.89572 |
| Compound **5.11** | | | | C | -3.54311 | -1.65229 | 0.23720 |
| This structure was assigned as correct. | | | | H | -3.86368 | -1.55469 | -0.80548 |
| B3LYP/6-31g(d) | | | | H | -2.95082 | -0.44628 | 1.92619 |
| Gas phase. | | | | H | -4.31907 | -2.22817 | 0.75933 |
| | | | | C | 0.19150 | 3.84419 | -0.63033 |
| Electronic Energy: -931.796163614 hartree. | | | | H | -0.35446 | 4.13955 | 0.27586 |
| | | | | H | -0.55378 | 3.76741 | -1.43437 |
| Free Energy: -931.354267 hartree. | | | | H | 0.87612 | 4.66084 | -0.88151 |
| | | | | H | 2.82785 | 3.42395 | -0.65214 |
| H | -0.61377 | 1.24568 | -1.07685 | C | -0.12779 | -3.03322 | -0.96449 |
| C | 0.11378 | 1.28793 | -0.25706 | H | 0.14377 | -3.72390 | -0.15856 |
| C | 2.31939 | 0.09195 | 0.35050 | H | 0.79048 | -2.67870 | -1.44154 |
| C | 2.27430 | 2.50148 | -0.47442 | H | -0.70511 | -3.58259 | -1.71410 |
| C | 3.09117 | 1.25103 | -0.30873 | O | -1.38529 | -1.16230 | -1.61047 |
| C | 0.93769 | 2.54527 | -0.44350 | H | -1.96876 | -0.44566 | -1.32022 |
| C | 0.91416 | -0.04789 | -0.29199 | ---------- | | | |
| H | 2.15683 | 0.37026 | 1.40291 | | | | |
| H | 3.46587 | 0.94465 | -1.29727 | Compound **5.11** | | | |

This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -931.811972396 hartree.
Free Energy: -931.369876 hartree.

| | | | |
|---|---|---|---|
| H | -0.60402 | 1.26118 | -1.08405 |
| C | 0.11880 | 1.29407 | -0.26015 |
| C | 2.32197 | 0.08993 | 0.34835 |
| C | 2.28771 | 2.49611 | -0.48136 |
| C | 3.09702 | 1.23935 | -0.32323 |
| C | 0.95025 | 2.54855 | -0.44184 |
| C | 0.91503 | -0.04568 | -0.29226 |
| H | 2.16475 | 0.37846 | 1.39876 |
| H | 3.45709 | 0.92518 | -1.31492 |
| H | 1.02046 | -0.37002 | -1.33133 |
| H | 4.00253 | 1.46515 | 0.25522 |
| C | 3.14287 | -1.23381 | 0.37547 |
| H | 2.47494 | -2.01730 | 0.75638 |
| C | 4.31760 | -1.14918 | 1.36442 |
| H | 5.06779 | -0.41507 | 1.04574 |
| H | 4.82613 | -2.11800 | 1.44824 |
| H | 3.97717 | -0.86488 | 2.36821 |
| C | 3.64447 | -1.70304 | -1.00156 |
| H | 2.85253 | -1.70354 | -1.75911 |
| H | 4.03352 | -2.72658 | -0.93341 |
| H | 4.46017 | -1.07316 | -1.37645 |
| C | -0.66514 | 1.23188 | 1.08194 |
| H | -0.10639 | 1.78363 | 1.85066 |
| C | -0.02831 | -0.99361 | 0.48785 |
| H | 0.53142 | -1.72212 | 1.08385 |
| O | -0.65805 | -0.14956 | 1.46741 |
| C | -2.13112 | 1.78743 | 1.09591 |
| H | -2.43121 | 1.85342 | 2.14943 |
| H | -2.13023 | 2.80982 | 0.70251 |
| C | -0.97718 | -1.86531 | -0.42958 |
| C | -2.22426 | -2.47404 | 0.29644 |
| H | -2.43076 | -3.44844 | -0.16436 |
| H | -1.96744 | -2.67301 | 1.34451 |
| C | -3.06966 | 0.87172 | 0.33818 |
| C | -3.56786 | 1.30987 | -1.02032 |
| H | -2.76391 | 1.63110 | -1.69757 |
| H | -4.22302 | 2.18571 | -0.90593 |
| H | -4.15457 | 0.53559 | -1.52594 |
| C | -3.28314 | -0.33352 | 0.89910 |
| C | -3.54641 | -1.65273 | 0.24228 |
| H | -3.87430 | -1.55324 | -0.79803 |
| H | -2.94918 | -0.44430 | 1.92862 |
| H | -4.31722 | -2.23182 | 0.76888 |
| C | 0.21129 | 3.85261 | -0.61728 |
| H | -0.33652 | 4.14091 | 0.29015 |
| H | -0.53225 | 3.78964 | -1.42423 |
| H | 0.90128 | 4.66910 | -0.85714 |
| H | 2.84620 | 3.41644 | -0.65783 |
| C | -0.12687 | -3.03068 | -0.95758 |
| H | 0.13750 | -3.72128 | -0.14923 |
| H | 0.79710 | -2.67915 | -1.42716 |
| H | -0.69708 | -3.58487 | -1.71041 |
| O | -1.39078 | -1.16297 | -1.61476 |
| H | -1.96418 | -0.43767 | -1.32389 |

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Compound **5.11**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -931.792591775 hartree.
Free Energy: -931.351184 hartree.

| | | | |
|---|---|---|---|
| H | -0.51384 | 1.36298 | -1.21652 |
| C | 0.13718 | 1.38871 | -0.33490 |
| C | 2.28262 | 0.11755 | 0.36325 |
| C | 2.35910 | 2.49597 | -0.51775 |
| C | 3.10633 | 1.20300 | -0.35424 |
| C | 1.02668 | 2.60600 | -0.48222 |
| C | 0.86685 | 0.01556 | -0.26884 |
| H | 2.14170 | 0.46382 | 1.39954 |
| H | 3.43186 | 0.84439 | -1.34315 |
| H | 0.96694 | -0.39094 | -1.28005 |
| H | 4.03061 | 1.39414 | 0.20494 |
| C | 3.04963 | -1.23545 | 0.45722 |
| H | 2.40071 | -1.93002 | 1.00963 |
| C | 4.33340 | -1.09909 | 1.29557 |
| H | 5.09958 | -0.51008 | 0.77816 |
| H | 4.76635 | -2.08603 | 1.49738 |
| H | 4.13478 | -0.61709 | 2.26079 |
| C | 3.35674 | -1.89798 | -0.89688 |
| H | 2.44368 | -2.11813 | -1.45690 |
| H | 3.88155 | -2.84796 | -0.73673 |
| H | 4.00813 | -1.27439 | -1.52013 |
| C | -0.78329 | 1.41198 | 0.91679 |
| H | -0.28966 | 1.97195 | 1.72387 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.10465 | -0.85155 | 0.56622 | C | -0.85931 | 0.01201 | 0.26257 |
| H | 0.46880 | -1.42850 | 1.30694 | H | -2.11402 | 0.47124 | -1.41015 |
| O | -0.89870 | 0.04727 | 1.34570 | H | -3.41234 | 0.82304 | 1.32962 |
| C | -2.21835 | 2.00913 | 0.68624 | H | -0.96442 | -0.41033 | 1.26786 |
| H | -2.57921 | 2.46191 | 1.61728 | H | -4.01036 | 1.38387 | -0.21814 |
| H | -2.15779 | 2.81019 | -0.05809 | C | -3.01094 | -1.22964 | -0.46171 |
| C | -0.91348 | -1.97817 | -0.18642 | H | -2.38389 | -1.91380 | -1.04979 |
| C | -1.68737 | -1.67129 | -1.50220 | C | -4.32988 | -1.08566 | -1.22616 |
| H | -1.04748 | -1.06595 | -2.15663 | H | -5.07533 | -0.53464 | -0.64180 |
| H | -1.77484 | -2.64735 | -1.99512 | H | -4.75427 | -2.07131 | -1.44639 |
| C | -3.12352 | 0.88278 | 0.23615 | H | -4.18944 | -0.55927 | -2.17751 |
| C | -3.96885 | 0.25347 | 1.31243 | C | -3.26211 | -1.89924 | 0.89239 |
| H | -4.69756 | 0.98857 | 1.68355 | H | -2.33095 | -2.10632 | 1.42655 |
| H | -3.35517 | -0.04800 | 2.16911 | H | -3.77427 | -2.85680 | 0.74225 |
| H | -4.53258 | -0.61441 | 0.95946 | H | -3.90618 | -1.28679 | 1.53315 |
| C | -2.95470 | 0.39482 | -1.00148 | C | 0.78371 | 1.41139 | -0.90129 |
| C | -3.10217 | -1.02891 | -1.44478 | H | 0.28651 | 1.98085 | -1.69958 |
| H | -3.52959 | -1.10178 | -2.45446 | C | 0.10479 | -0.83946 | -0.58164 |
| H | -2.38124 | 1.00269 | -1.70275 | H | -0.46842 | -1.40801 | -1.32998 |
| H | -3.75564 | -1.60720 | -0.78413 | O | 0.90416 | 0.05872 | -1.34001 |
| C | 0.34597 | 3.94314 | -0.64936 | C | 2.20536 | 2.00854 | -0.65230 |
| H | -0.21987 | 4.23168 | 0.24675 | H | 2.57933 | 2.47366 | -1.57083 |
| H | -0.37237 | 3.92815 | -1.48125 | H | 2.13316 | 2.79081 | 0.11035 |
| H | 1.07542 | 4.73491 | -0.84833 | C | 0.89640 | -1.95952 | 0.16759 |
| H | 2.95847 | 3.39179 | -0.68167 | C | 1.63355 | -1.65730 | 1.49489 |
| C | -1.80203 | -2.71920 | 0.81956 | H | 0.99407 | -1.02684 | 2.12670 |
| H | -2.55628 | -2.06297 | 1.25639 | H | 1.69247 | -2.63088 | 1.99627 |
| H | -1.19418 | -3.11287 | 1.64524 | C | 3.09244 | 0.86956 | -0.21152 |
| H | -2.29953 | -3.56539 | 0.33330 | C | 3.91256 | 0.23301 | -1.29724 |
| O | 0.10322 | -2.89228 | -0.66687 | H | 4.65376 | 0.95598 | -1.66324 |
| H | 0.57562 | -3.24076 | 0.10678 | H | 3.28086 | -0.03698 | -2.15034 |
| ---------- | | | | H | 4.45505 | -0.65401 | -0.96068 |
| | | | | C | 2.91605 | 0.37587 | 1.01822 |
| Compound **5.11** | | | | C | 3.05411 | -1.05076 | 1.44731 |
| This structure was assigned as incorrect. | | | | H | 3.48235 | -1.13627 | 2.45343 |
| M06-2X/6-31g(d) | | | | H | 2.35339 | 0.98584 | 1.72601 |
| SMD implicit solvation in THF was used. | | | | H | 3.69217 | -1.63230 | 0.77468 |
| | | | | C | -0.31851 | 3.91373 | 0.61716 |
| Electronic Energy: -931.404826513 hartree. | | | | H | 0.23282 | 4.17416 | -0.29564 |
| | | | | H | 0.41398 | 3.89548 | 1.43443 |
| Free Energy: -930.957994 hartree. | | | | H | -1.03501 | 4.71636 | 0.81520 |
| | | | | H | -2.93940 | 3.38461 | 0.66046 |
| H | 0.51663 | 1.34560 | 1.22931 | C | 1.81842 | -2.66146 | -0.82288 |
| C | -0.12956 | 1.37147 | 0.34485 | H | 2.56133 | -1.97271 | -1.22974 |
| C | -2.25997 | 0.12062 | -0.37467 | H | 1.23415 | -3.05760 | -1.66298 |
| C | -2.34492 | 2.48320 | 0.51089 | H | 2.33165 | -3.49833 | -0.33731 |
| C | -3.08971 | 1.19023 | 0.34414 | O | -0.11744 | -2.88120 | 0.60210 |
| C | -1.01480 | 2.58637 | 0.48000 | H | -0.61525 | -3.16630 | -0.18239 |

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Compound **5.11**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -931.808409013 hartree.
Free Energy: -931.368150 hartree.

| | | | |
|---|---|---|---|
| H | -0.51650 | 1.36026 | -1.21463 |
| C | 0.13630 | 1.38582 | -0.33512 |
| C | 2.28439 | 0.11751 | 0.36331 |
| C | 2.35787 | 2.49625 | -0.52080 |
| C | 3.10775 | 1.20521 | -0.35130 |
| C | 1.02400 | 2.60487 | -0.48617 |
| C | 0.86910 | 0.01397 | -0.27114 |
| H | 2.14168 | 0.46070 | 1.40029 |
| H | 3.43985 | 0.84657 | -1.33801 |
| H | 0.97070 | -0.38841 | -1.28378 |
| H | 4.02895 | 1.40102 | 0.21172 |
| C | 3.05329 | -1.23453 | 0.45698 |
| H | 2.40125 | -1.93529 | 0.99656 |
| C | 4.32858 | -1.10185 | 1.30761 |
| H | 5.09975 | -0.50595 | 0.80474 |
| H | 4.76222 | -2.08990 | 1.50642 |
| H | 4.11985 | -0.62923 | 2.27602 |
| C | 3.37719 | -1.88579 | -0.89781 |
| H | 2.47228 | -2.08272 | -1.48038 |
| H | 3.88008 | -2.84858 | -0.73992 |
| H | 4.05075 | -1.26792 | -1.50377 |
| C | -0.78034 | 1.40875 | 0.91911 |
| H | -0.28657 | 1.97025 | 1.72467 |
| C | -0.10102 | -0.85708 | 0.56122 |
| H | 0.47201 | -1.43929 | 1.29711 |
| O | -0.89005 | 0.04199 | 1.35054 |
| C | -2.21580 | 2.00531 | 0.69628 |
| H | -2.57297 | 2.45302 | 1.63116 |
| H | -2.15482 | 2.81020 | -0.04358 |
| C | -0.91745 | -1.97866 | -0.19272 |
| C | -1.69132 | -1.66593 | -1.50658 |
| H | -1.05317 | -1.05663 | -2.15904 |
| H | -1.78479 | -2.63966 | -2.00376 |
| C | -3.12512 | 0.88308 | 0.24281 |
| C | -3.97788 | 0.25555 | 1.31373 |
| H | -4.70713 | 0.99183 | 1.68348 |
| H | -3.37227 | -0.04696 | 2.17606 |
| H | -4.54160 | -0.61231 | 0.95967 |
| C | -2.95416 | 0.39665 | -0.99619 |
| C | -3.10617 | -1.02481 | -1.44529 |
| H | -3.53145 | -1.09204 | -2.45663 |
| H | -2.37130 | 1.00208 | -1.69153 |
| H | -3.75973 | -1.60643 | -0.78753 |
| C | 0.34147 | 3.94034 | -0.65673 |
| H | -0.21709 | 4.23467 | 0.24236 |
| H | -0.38416 | 3.92042 | -1.48206 |
| H | 1.06917 | 4.73209 | -0.86616 |
| H | 2.95626 | 3.39262 | -0.68857 |
| C | -1.80621 | -2.71668 | 0.81424 |
| H | -2.56091 | -2.06007 | 1.25113 |
| H | -1.19747 | -3.11388 | 1.63761 |
| H | -2.30929 | -3.56175 | 0.33053 |
| O | 0.09446 | -2.90109 | -0.67343 |
| H | 0.59429 | -3.21374 | 0.10039 |

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Compound **5.11**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -931.407927631 hartree.
Free Energy: -930.962926 hartree.

| | | | |
|---|---|---|---|
| H | -1.36594 | 1.38787 | 1.09067 |
| C | -1.08041 | 1.12433 | 0.06314 |
| C | -1.42115 | -1.45842 | -0.20045 |
| C | -2.87096 | 0.23896 | -1.43558 |
| C | -2.39240 | -1.18392 | -1.36048 |
| C | -2.30673 | 1.27832 | -0.81284 |
| C | -0.44988 | -0.28066 | -0.00576 |
| H | -0.79753 | -2.31282 | -0.48795 |
| H | -3.26184 | -1.84974 | -1.27131 |
| H | 0.10815 | -0.43880 | 0.91806 |
| H | -1.92281 | -1.45455 | -2.31777 |
| C | -2.15602 | -1.91804 | 1.08067 |
| H | -2.70144 | -2.82570 | 0.78217 |
| C | -3.19380 | -0.94129 | 1.63558 |
| H | -2.72736 | -0.01835 | 1.99875 |
| H | -3.71747 | -1.39641 | 2.48434 |
| H | -3.94322 | -0.66988 | 0.88630 |
| C | -1.17497 | -2.33060 | 2.18052 |
| H | -0.39843 | -3.00041 | 1.79193 |
| H | -1.69881 | -2.85673 | 2.98621 |

| | | | |
|---|---|---|---|
| H | -0.67912 | -1.46233 | 2.63085 |
| C | 0.08369 | 2.03883 | -0.37991 |
| H | -0.28584 | 2.88742 | -0.96555 |
| C | 0.56461 | -0.13562 | -1.15547 |
| H | 0.06660 | -0.40321 | -2.10509 |
| O | 0.88413 | 1.25019 | -1.25513 |
| C | 0.93668 | 2.62694 | 0.77936 |
| H | 1.61222 | 3.36776 | 0.33703 |
| H | 0.26836 | 3.16035 | 1.46669 |
| C | 1.82218 | -1.06716 | -1.11992 |
| C | 2.47449 | -1.36986 | 0.24717 |
| H | 1.68303 | -1.62556 | 0.96072 |
| H | 3.05218 | -2.28916 | 0.09424 |
| C | 1.73094 | 1.53806 | 1.45589 |
| C | 1.20763 | 0.96605 | 2.74584 |
| H | 0.12784 | 0.77863 | 2.69930 |
| H | 1.35866 | 1.68269 | 3.56411 |
| H | 1.70669 | 0.03247 | 3.02363 |
| C | 2.76600 | 1.05309 | 0.76125 |
| C | 3.39848 | -0.30251 | 0.87147 |
| H | 3.60014 | -0.59161 | 1.90906 |
| H | 3.03949 | 1.61126 | -0.13132 |
| H | 4.36331 | -0.30219 | 0.35241 |
| C | -2.90817 | 2.65796 | -0.89411 |
| H | -2.28654 | 3.35155 | -1.47197 |
| H | -3.01927 | 3.09209 | 0.10790 |
| H | -3.89535 | 2.62869 | -1.36448 |
| H | -3.76055 | 0.41848 | -2.04059 |
| C | 2.85175 | -0.58461 | -2.13848 |
| H | 3.25062 | 0.39911 | -1.88436 |
| H | 2.39219 | -0.50864 | -3.13194 |
| H | 3.67611 | -1.30316 | -2.19676 |
| O | 1.35492 | -2.36520 | -1.52255 |
| H | 0.95172 | -2.26816 | -2.40126 |

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Compound **5.12**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +227.808655 kJ.

| | | | |
|---|---|---|---|
| H | 4.77210 | -2.31400 | 1.71730 |
| C | 4.94190 | -1.30090 | 2.07240 |
| C | 6.98850 | 0.14240 | 2.68240 |
| C | 5.72110 | 0.49840 | 0.50070 |
| C | 7.02820 | 0.69300 | 1.23820 |
| C | 4.77050 | -0.37640 | 0.87020 |
| C | 6.34280 | -1.27310 | 2.70370 |
| H | 6.31650 | 0.79480 | 3.24360 |
| H | 7.81120 | 0.21440 | 0.65110 |
| H | 6.99100 | -1.94810 | 2.14460 |
| H | 7.24490 | 1.76110 | 1.24810 |
| C | 8.37620 | 0.22970 | 3.38680 |
| H | 8.23820 | -0.04850 | 4.43040 |
| C | 8.92000 | 1.66800 | 3.43590 |
| H | 9.21360 | 2.02660 | 2.44920 |
| H | 9.80060 | 1.73050 | 4.07590 |
| H | 8.17760 | 2.35860 | 3.83720 |
| C | 9.43650 | -0.73020 | 2.81530 |
| H | 9.12560 | -1.77210 | 2.89020 |
| H | 10.37390 | -0.64330 | 3.36540 |
| H | 9.65720 | -0.52110 | 1.76900 |
| C | 3.99980 | -0.99030 | 3.25300 |
| H | 3.78580 | 0.07950 | 3.25030 |
| C | 6.05280 | -1.80470 | 4.12390 |
| H | 6.77580 | -1.44250 | 4.85010 |
| O | 4.77450 | -1.23790 | 4.43830 |
| C | 2.64210 | -1.75700 | 3.28750 |
| H | 1.99850 | -1.28380 | 4.03010 |
| H | 2.10820 | -1.68340 | 2.34140 |
| C | 6.06230 | -3.35470 | 4.26400 |
| O | 6.52820 | -4.07620 | 3.38200 |
| C | 5.49860 | -4.00000 | 5.54720 |
| H | 6.18530 | -4.78590 | 5.86060 |
| H | 5.50860 | -3.24610 | 6.33440 |
| C | 2.82480 | -3.21010 | 3.68400 |
| C | 2.97330 | -4.22000 | 2.55680 |
| H | 4.00190 | -4.28820 | 2.20650 |
| H | 2.33480 | -3.95860 | 1.71300 |
| H | 2.67390 | -5.21330 | 2.89100 |
| C | 3.15350 | -3.46640 | 4.96160 |
| C | 4.06950 | -4.58320 | 5.39760 |
| H | 4.07030 | -5.41120 | 4.68920 |
| H | 3.08100 | -2.66120 | 5.68040 |
| H | 3.71930 | -4.98010 | 6.35030 |
| C | 3.48130 | -0.52360 | 0.08520 |
| H | 2.63270 | -0.17890 | 0.67500 |
| H | 3.31680 | -1.56680 | -0.18600 |
| H | 3.50520 | 0.06260 | -0.83390 |
| H | 5.57920 | 1.10900 | -0.37960 |

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Compound **5.12**

This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +259.412415 kJ.

| | | | |
|---|---|---|---|
| H | 4.95940 | -1.47590 | 1.08670 |
| C | 4.83070 | -0.89910 | 2.00100 |
| C | 7.23780 | -0.48070 | 2.97430 |
| C | 5.83470 | 1.41790 | 1.98170 |
| C | 6.99450 | 1.04210 | 2.88090 |
| C | 4.87210 | 0.57090 | 1.57390 |
| C | 5.90550 | -1.27300 | 3.03350 |
| H | 7.72620 | -0.62750 | 3.93940 |
| H | 7.89260 | 1.55390 | 2.53360 |
| H | 6.12930 | -2.31830 | 2.87520 |
| H | 6.78140 | 1.45060 | 3.86940 |
| C | 8.28060 | -1.00030 | 1.94140 |
| H | 9.14180 | -0.33400 | 2.01610 |
| C | 7.82730 | -0.95230 | 0.47280 |
| H | 7.03550 | -1.67100 | 0.26850 |
| H | 8.65540 | -1.19330 | -0.19430 |
| H | 7.47050 | 0.03760 | 0.19050 |
| C | 8.81520 | -2.39990 | 2.29510 |
| H | 9.15970 | -2.44640 | 3.32870 |
| H | 9.66380 | -2.66110 | 1.66190 |
| H | 8.06320 | -3.17640 | 2.15710 |
| C | 3.51410 | -1.31780 | 2.69550 |
| H | 2.71460 | -0.61370 | 2.47370 |
| C | 5.16990 | -1.12860 | 4.37900 |
| H | 5.31410 | -0.11200 | 4.74410 |
| O | 3.76920 | -1.23450 | 4.10020 |
| C | 2.97660 | -2.73530 | 2.32180 |
| H | 1.97850 | -2.85160 | 2.74650 |
| H | 2.85730 | -2.83700 | 1.24270 |
| C | 5.59560 | -2.08600 | 5.53060 |
| O | 5.53610 | -1.69990 | 6.69650 |
| C | 6.10080 | -3.52370 | 5.24380 |
| H | 6.78380 | -3.50330 | 4.39840 |
| H | 6.71690 | -3.82840 | 6.08970 |
| C | 3.85160 | -3.84960 | 2.86860 |
| C | 4.80790 | -4.50240 | 1.88050 |
| H | 4.23400 | -5.02710 | 1.11640 |
| H | 5.46360 | -5.23300 | 2.35060 |
| H | 5.43090 | -3.76980 | 1.37130 |
| C | 3.86420 | -4.04380 | 4.19970 |
| C | 5.00580 | -4.60410 | 5.01340 |
| H | 5.43360 | -5.48560 | 4.53820 |
| H | 3.14910 | -3.49130 | 4.79560 |
| H | 4.60560 | -4.93760 | 5.97160 |
| C | 3.79640 | 1.02700 | 0.60270 |
| H | 2.81990 | 1.07950 | 1.08240 |
| H | 3.73170 | 0.34030 | -0.24160 |
| H | 4.01620 | 2.01890 | 0.20640 |
| H | 5.81260 | 2.44810 | 1.65600 |

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Compound **5.12**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -891.289473685 hartree.
Free Energy: -890.900478 hartree.

| | | | |
|---|---|---|---|
| H | 4.71735 | -2.25249 | 1.67108 |
| C | 4.89760 | -1.23762 | 2.04588 |
| C | 6.99261 | 0.14338 | 2.68195 |
| C | 5.73492 | 0.53239 | 0.51010 |
| C | 7.04776 | 0.66187 | 1.23260 |
| C | 4.74578 | -0.29271 | 0.87238 |
| C | 6.30000 | -1.23929 | 2.71655 |
| H | 6.35197 | 0.84023 | 3.24409 |
| H | 7.82775 | 0.13043 | 0.66471 |
| H | 6.93206 | -1.98104 | 2.22236 |
| H | 7.35260 | 1.71577 | 1.22934 |
| C | 8.38362 | 0.16238 | 3.38279 |
| H | 8.21508 | -0.13345 | 4.42797 |
| C | 8.97712 | 1.58090 | 3.43282 |
| H | 9.28875 | 1.92869 | 2.44099 |
| H | 9.86288 | 1.60469 | 4.07835 |
| H | 8.25451 | 2.30413 | 3.83030 |
| C | 9.40649 | -0.82838 | 2.79963 |
| H | 9.05165 | -1.86401 | 2.83648 |
| H | 10.34243 | -0.78238 | 3.36908 |
| H | 9.65170 | -0.59587 | 1.75649 |
| C | 3.90569 | -0.97379 | 3.21942 |
| H | 3.58457 | 0.07582 | 3.20324 |
| C | 5.95112 | -1.70851 | 4.13533 |
| H | 6.63471 | -1.31079 | 4.89761 |
| O | 4.67087 | -1.13704 | 4.43004 |
| C | 2.61953 | -1.86126 | 3.25283 |
| H | 1.94898 | -1.42470 | 4.00308 |
| H | 2.11268 | -1.77742 | 2.28382 |

| | | | |
|---|---|---|---|
| C | 5.98782 | -3.25489 | 4.31074 |
| O | 6.43089 | -3.97537 | 3.43369 |
| C | 5.51766 | -3.86573 | 5.63755 |
| H | 6.28394 | -4.58095 | 5.96070 |
| H | 5.41900 | -3.08886 | 6.40370 |
| C | 2.93865 | -3.29571 | 3.61985 |
| C | 3.07055 | -4.32318 | 2.51859 |
| H | 3.98864 | -4.20640 | 1.92870 |
| H | 2.22754 | -4.23951 | 1.82051 |
| H | 3.07171 | -5.34281 | 2.91428 |
| C | 3.22866 | -3.52864 | 4.91093 |
| C | 4.15037 | -4.58560 | 5.44844 |
| H | 4.28329 | -5.42083 | 4.75435 |
| H | 3.04130 | -2.71745 | 5.61328 |
| H | 3.82150 | -4.99406 | 6.41221 |
| C | 3.45073 | -0.35975 | 0.10044 |
| H | 2.59343 | -0.04670 | 0.71212 |
| H | 3.23734 | -1.38384 | -0.23644 |
| H | 3.47989 | 0.28794 | -0.78171 |
| H | 5.60041 | 1.15925 | -0.37174 |

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Compound **5.12**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -890.921799599 hartree.
Free Energy: -890.526294 hartree.

| | | | |
|---|---|---|---|
| H | 4.70941 | -2.28723 | 1.74471 |
| C | 4.91666 | -1.26230 | 2.07865 |
| C | 6.94425 | 0.15904 | 2.68486 |
| C | 5.73428 | 0.46365 | 0.49587 |
| C | 7.03611 | 0.63392 | 1.23032 |
| C | 4.75060 | -0.35102 | 0.88756 |
| C | 6.32322 | -1.24538 | 2.70669 |
| H | 6.24647 | 0.83880 | 3.19915 |
| H | 7.83895 | 0.09562 | 0.70298 |
| H | 6.97483 | -1.94622 | 2.17770 |
| H | 7.31679 | 1.69287 | 1.20029 |
| C | 8.29302 | 0.24344 | 3.43711 |
| H | 8.07257 | 0.12083 | 4.50586 |
| C | 8.94435 | 1.61917 | 3.27909 |
| H | 9.33180 | 1.76592 | 2.26453 |
| H | 9.78765 | 1.72539 | 3.96987 |
| H | 8.23330 | 2.42673 | 3.48939 |
| C | 9.27845 | -0.86094 | 3.04607 |
| H | 8.90831 | -1.85695 | 3.31276 |
| H | 10.23471 | -0.71751 | 3.56130 |
| H | 9.48167 | -0.85713 | 1.96843 |
| C | 3.97692 | -0.94313 | 3.26835 |
| H | 3.70609 | 0.12107 | 3.25370 |
| C | 6.01038 | -1.74685 | 4.11271 |
| H | 6.73402 | -1.41185 | 4.86778 |
| O | 4.76090 | -1.15044 | 4.45345 |
| C | 2.66961 | -1.77378 | 3.32689 |
| H | 2.04762 | -1.34842 | 4.12273 |
| H | 2.13089 | -1.64319 | 2.38155 |
| C | 5.97707 | -3.28974 | 4.21445 |
| O | 6.31718 | -3.98712 | 3.28007 |
| C | 5.55429 | -3.93522 | 5.53127 |
| H | 6.32481 | -4.66270 | 5.80985 |
| H | 5.48375 | -3.17914 | 6.31977 |
| C | 2.97435 | -3.22209 | 3.62606 |
| C | 3.11222 | -4.20632 | 2.48712 |
| H | 4.14022 | -4.27851 | 2.11197 |
| H | 2.47384 | -3.91377 | 1.64665 |
| H | 2.81392 | -5.21295 | 2.79631 |
| C | 3.27700 | -3.51699 | 4.89646 |
| C | 4.18245 | -4.62519 | 5.34522 |
| H | 4.27586 | -5.41057 | 4.58890 |
| H | 3.12099 | -2.73781 | 5.64242 |
| H | 3.87078 | -5.08540 | 6.28844 |
| C | 3.43822 | -0.43044 | 0.15616 |
| H | 2.61495 | -0.06031 | 0.78086 |
| H | 3.19443 | -1.46697 | -0.11007 |
| H | 3.45635 | 0.16678 | -0.76031 |
| H | 5.58957 | 1.06710 | -0.40042 |

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Compound **5.12**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -891.306314088 hartree.
Free Energy: -890.917099 hartree.

| | | | |
|---|---|---|---|
| H | 4.73572 | -2.28477 | 1.70975 |
| C | 4.92166 | -1.26246 | 2.05861 |
| C | 6.99849 | 0.14035 | 2.68287 |
| C | 5.75466 | 0.48391 | 0.49456 |
| C | 7.05852 | 0.64364 | 1.22827 |

| | | | |
|---|---|---|---|
| C | 4.76799 | -0.34333 | 0.86419 |
| C | 6.32926 | -1.25431 | 2.71776 |
| H | 6.33756 | 0.82982 | 3.22980 |
| H | 7.85355 | 0.11967 | 0.67440 |
| H | 6.96941 | -1.98166 | 2.21239 |
| H | 7.34407 | 1.70300 | 1.21413 |
| C | 8.37913 | 0.19988 | 3.40123 |
| H | 8.20289 | -0.08295 | 4.44822 |
| C | 8.94184 | 1.63080 | 3.43571 |
| H | 9.26462 | 1.97128 | 2.44449 |
| H | 9.81581 | 1.68386 | 4.09676 |
| H | 8.19918 | 2.34668 | 3.81046 |
| C | 9.43149 | -0.77519 | 2.84698 |
| H | 9.10368 | -1.81929 | 2.90306 |
| H | 10.36083 | -0.69549 | 3.42479 |
| H | 9.68208 | -0.55963 | 1.80103 |
| C | 3.94424 | -0.96973 | 3.23748 |
| H | 3.65523 | 0.08904 | 3.22347 |
| C | 5.99139 | -1.74070 | 4.13238 |
| H | 6.68780 | -1.36503 | 4.89364 |
| O | 4.71745 | -1.15831 | 4.44340 |
| C | 2.62846 | -1.81156 | 3.28670 |
| H | 1.99021 | -1.35901 | 4.05576 |
| H | 2.10611 | -1.69595 | 2.32982 |
| C | 6.01886 | -3.28904 | 4.29200 |
| O | 6.48160 | -4.00222 | 3.41642 |
| C | 5.53048 | -3.91149 | 5.60427 |
| H | 6.28069 | -4.64748 | 5.91838 |
| H | 5.44946 | -3.14609 | 6.38341 |
| C | 2.90587 | -3.26169 | 3.62687 |
| C | 2.92541 | -4.27482 | 2.50874 |
| H | 3.64647 | -4.02915 | 1.71924 |
| H | 1.93980 | -4.30931 | 2.02216 |
| H | 3.15184 | -5.28428 | 2.86403 |
| C | 3.24145 | -3.51944 | 4.90306 |
| C | 4.14863 | -4.60236 | 5.41100 |
| H | 4.25567 | -5.43091 | 4.70449 |
| H | 3.10626 | -2.70719 | 5.61606 |
| H | 3.82366 | -5.01869 | 6.37280 |
| C | 3.48014 | -0.43531 | 0.08326 |
| H | 2.61655 | -0.11008 | 0.67952 |
| H | 3.27230 | -1.46821 | -0.22935 |
| H | 3.51470 | 0.19026 | -0.81543 |
| H | 5.62292 | 1.09174 | -0.40154 |

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Compound **5.12**
This structure was assigned as incorrect.

B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -891.279337099 hartree.
Free Energy: -890.889731 hartree.

| | | | |
|---|---|---|---|
| H | 4.56853 | -2.38443 | 2.10453 |
| C | 4.83416 | -1.33539 | 2.27964 |
| C | 7.06250 | -0.05112 | 2.60758 |
| C | 5.79153 | 0.00319 | 0.41081 |
| C | 7.13097 | 0.13546 | 1.08069 |
| C | 4.74000 | -0.62861 | 0.94381 |
| C | 6.23869 | -1.31955 | 2.95300 |
| H | 6.50035 | 0.80630 | 3.00798 |
| H | 7.83180 | -0.58966 | 0.63765 |
| H | 6.80626 | -2.19899 | 2.62766 |
| H | 7.54951 | 1.12263 | 0.84929 |
| C | 8.46737 | -0.00834 | 3.27995 |
| H | 8.30676 | -0.11590 | 4.36107 |
| C | 9.14806 | 1.35757 | 3.08387 |
| H | 9.44614 | 1.52160 | 2.04166 |
| H | 10.05512 | 1.42579 | 3.69562 |
| H | 8.48493 | 2.18021 | 3.37723 |
| C | 9.41745 | -1.14262 | 2.85722 |
| H | 8.99197 | -2.13620 | 3.03803 |
| H | 10.35154 | -1.08248 | 3.42775 |
| H | 9.68272 | -1.08152 | 1.79528 |
| C | 3.86511 | -0.78142 | 3.36700 |
| H | 3.60373 | 0.25917 | 3.13376 |
| C | 5.89064 | -1.40158 | 4.45044 |
| H | 6.58143 | -0.81927 | 5.06731 |
| O | 4.62135 | -0.74535 | 4.58833 |
| C | 2.54235 | -1.59490 | 3.57217 |
| H | 1.79009 | -0.93710 | 4.02332 |
| H | 2.15907 | -1.89866 | 2.59078 |
| C | 5.86801 | -2.78977 | 5.17790 |
| O | 5.90239 | -2.76109 | 6.39448 |
| C | 5.80081 | -4.15857 | 4.48080 |
| H | 6.04468 | -4.08992 | 3.41535 |
| H | 6.55204 | -4.79699 | 4.96173 |
| C | 2.82270 | -2.78758 | 4.46400 |
| C | 2.55646 | -2.58365 | 5.93479 |
| H | 1.49206 | -2.35130 | 6.08089 |
| H | 3.13187 | -1.73773 | 6.32369 |
| H | 2.79020 | -3.46489 | 6.53661 |
| C | 3.43485 | -3.86065 | 3.93507 |
| C | 4.38307 | -4.78484 | 4.64878 |

| | | | |
|---|---|---|---|
| H | 4.38450 | -5.79522 | 4.22200 |
| H | 3.49635 | -3.92312 | 2.84753 |
| H | 4.16723 | -4.87325 | 5.71716 |
| C | 3.41967 | -0.71882 | 0.21834 |
| H | 2.61158 | -0.22739 | 0.77709 |
| H | 3.11011 | -1.76397 | 0.07605 |
| H | 3.47541 | -0.24602 | -0.76739 |
| H | 5.69087 | 0.45381 | -0.57667 |

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Compound **5.12**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -890.913347876 hartree.
Free Energy: -890.518202 hartree.

| | | | |
|---|---|---|---|
| H | 4.57503 | -2.38478 | 2.15192 |
| C | 4.85173 | -1.33641 | 2.30808 |
| C | 7.01281 | -0.01068 | 2.62447 |
| C | 5.79802 | -0.03572 | 0.41794 |
| C | 7.12553 | 0.13562 | 1.10308 |
| C | 4.74895 | -0.65217 | 0.96779 |
| C | 6.25386 | -1.31085 | 2.94944 |
| H | 6.39247 | 0.82756 | 2.97957 |
| H | 7.85483 | -0.58630 | 0.70353 |
| H | 6.84595 | -2.16085 | 2.59219 |
| H | 7.51985 | 1.12693 | 0.85411 |
| C | 8.37892 | 0.10204 | 3.34341 |
| H | 8.17121 | 0.24911 | 4.41087 |
| C | 9.16172 | 1.33339 | 2.88126 |
| H | 9.54869 | 1.20772 | 1.86377 |
| H | 10.01959 | 1.50846 | 3.53920 |
| H | 8.53797 | 2.23494 | 2.89733 |
| C | 9.24310 | -1.15520 | 3.21577 |
| H | 8.78744 | -2.02143 | 3.70853 |
| H | 10.22063 | -0.99178 | 3.68248 |
| H | 9.41954 | -1.41925 | 2.16590 |
| C | 3.91728 | -0.75235 | 3.39718 |
| H | 3.67584 | 0.29201 | 3.15946 |
| C | 5.92444 | -1.43303 | 4.43681 |
| H | 6.65438 | -0.91447 | 5.06668 |
| O | 4.69198 | -0.73159 | 4.60363 |
| C | 2.59215 | -1.53834 | 3.61322 |
| H | 1.86632 | -0.88792 | 4.11385 |
| H | 2.18259 | -1.80138 | 2.63100 |
| C | 5.82760 | -2.84239 | 5.08572 |
| O | 5.77487 | -2.87383 | 6.29837 |
| C | 5.78589 | -4.16556 | 4.32074 |
| H | 5.99284 | -4.02899 | 3.25512 |
| H | 6.56396 | -4.81194 | 4.74292 |
| C | 2.88784 | -2.76279 | 4.44692 |
| C | 2.71559 | -2.59116 | 5.93197 |
| H | 1.65501 | -2.40602 | 6.14860 |
| H | 3.28085 | -1.72555 | 6.28777 |
| H | 3.02951 | -3.46824 | 6.50152 |
| C | 3.43268 | -3.83653 | 3.85785 |
| C | 4.38576 | -4.80361 | 4.50306 |
| H | 4.36649 | -5.78859 | 4.02689 |
| H | 3.42912 | -3.87469 | 2.76803 |
| H | 4.19773 | -4.93798 | 5.57164 |
| C | 3.41716 | -0.74740 | 0.27440 |
| H | 2.63583 | -0.22577 | 0.84260 |
| H | 3.09384 | -1.79221 | 0.17910 |
| H | 3.45619 | -0.30579 | -0.72571 |
| H | 5.69340 | 0.39370 | -0.57837 |

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Compound **5.12**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -891.297792814 hartree.
Free Energy: -890.907684 hartree.

| | | | |
|---|---|---|---|
| H | 4.56896 | -2.37680 | 2.09753 |
| C | 4.82827 | -1.32830 | 2.28088 |
| C | 7.06349 | -0.04633 | 2.60934 |
| C | 5.78573 | 0.01860 | 0.41604 |
| C | 7.12718 | 0.14574 | 1.08307 |
| C | 4.73266 | -0.61411 | 0.94805 |
| C | 6.23260 | -1.31023 | 2.95536 |
| H | 6.51216 | 0.81575 | 3.01514 |
| H | 7.82568 | -0.57844 | 0.63503 |
| H | 6.79814 | -2.19164 | 2.63532 |
| H | 7.54627 | 1.13331 | 0.85395 |
| C | 8.47237 | -0.02000 | 3.27491 |
| H | 8.31520 | -0.12499 | 4.35676 |
| C | 9.16968 | 1.33590 | 3.07337 |
| H | 9.46971 | 1.49490 | 2.03052 |
| H | 10.07874 | 1.39488 | 3.68462 |
| H | 8.51880 | 2.16972 | 3.36533 |

| | | | |
|---|---|---|---|
| C | 9.40545 | -1.16663 | 2.84973 |
| H | 8.97009 | -2.15433 | 3.04115 |
| H | 10.34582 | -1.11403 | 3.41229 |
| H | 9.66303 | -1.11684 | 1.78485 |
| C | 3.85129 | -0.78764 | 3.36634 |
| H | 3.58212 | 0.25215 | 3.14032 |
| C | 5.88717 | -1.38691 | 4.45291 |
| H | 6.57233 | -0.78794 | 5.06039 |
| O | 4.60362 | -0.75436 | 4.59467 |
| C | 2.53377 | -1.61073 | 3.56041 |
| H | 1.77152 | -0.95922 | 4.00414 |
| H | 2.16494 | -1.91620 | 2.57457 |
| C | 5.89233 | -2.76909 | 5.18892 |
| O | 5.96078 | -2.73042 | 6.40711 |
| C | 5.82159 | -4.13852 | 4.50109 |
| H | 6.06560 | -4.07076 | 3.43654 |
| H | 6.57318 | -4.77638 | 4.98251 |
| C | 2.81442 | -2.80171 | 4.45473 |
| C | 2.51741 | -2.60539 | 5.92021 |
| H | 1.44477 | -2.40156 | 6.05159 |
| H | 3.05882 | -1.74098 | 6.31887 |
| H | 2.76365 | -3.47993 | 6.52824 |
| C | 3.45770 | -3.86263 | 3.93734 |
| C | 4.40718 | -4.77377 | 4.66491 |
| H | 4.42513 | -5.78441 | 4.23928 |
| H | 3.54657 | -3.91791 | 2.85175 |
| H | 4.18040 | -4.86436 | 5.73126 |
| C | 3.41203 | -0.69920 | 0.22283 |
| H | 2.60532 | -0.20441 | 0.78092 |
| H | 3.09746 | -1.74277 | 0.08020 |
| H | 3.46977 | -0.22594 | -0.76346 |
| H | 5.68410 | 0.47277 | -0.57023 |

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Compound **5.13**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +193.560471 kJ.

| | | | |
|---|---|---|---|
| H | 3.75740 | -0.27840 | -1.47000 |
| C | 3.82190 | 0.80940 | -1.43220 |
| C | 5.15260 | 2.70110 | -2.62080 |
| C | 2.61960 | 2.84290 | -2.44770 |
| C | 3.84140 | 3.09940 | -3.33380 |
| C | 2.55720 | 1.37860 | -2.06560 |
| C | 5.11520 | 1.21310 | -2.15230 |
| H | 5.20230 | 3.30710 | -1.71410 |
| H | 2.67020 | 3.45410 | -1.54630 |
| H | 3.72790 | 2.53710 | -4.26110 |
| H | 5.25340 | 0.56440 | -3.01670 |
| H | 1.70980 | 3.13890 | -2.97170 |
| H | 3.85790 | 4.15300 | -3.61020 |
| C | 1.48150 | 0.62230 | -2.33990 |
| H | 0.60830 | 1.04190 | -2.81750 |
| H | 1.45610 | -0.43040 | -2.10430 |
| C | 6.41870 | 3.05200 | -3.45780 |
| H | 7.28840 | 2.67490 | -2.92170 |
| C | 6.63940 | 4.57050 | -3.56840 |
| H | 5.87170 | 5.05290 | -4.17290 |
| H | 7.60110 | 4.79160 | -4.03240 |
| H | 6.63810 | 5.04440 | -2.58630 |
| C | 6.45730 | 2.39960 | -4.85260 |
| H | 6.36920 | 1.31500 | -4.80120 |
| H | 7.40150 | 2.61550 | -5.35350 |
| H | 5.66120 | 2.77000 | -5.49820 |
| C | 4.08480 | 1.25620 | 0.02000 |
| H | 3.72280 | 2.27560 | 0.15410 |
| C | 6.15140 | 0.92980 | -1.04360 |
| H | 7.06020 | 1.51350 | -1.17540 |
| O | 5.50290 | 1.35620 | 0.15260 |
| C | 3.46860 | 0.39200 | 1.14850 |
| H | 3.84940 | 0.73090 | 2.11210 |
| H | 2.39660 | 0.58880 | 1.18330 |
| C | 6.59150 | -0.54550 | -0.92120 |
| O | 6.51590 | -1.32020 | -1.87490 |
| C | 7.16870 | -1.03600 | 0.41490 |
| H | 7.57650 | -2.03190 | 0.24270 |
| H | 8.01300 | -0.39990 | 0.67900 |
| C | 3.67090 | -1.11930 | 1.03810 |
| C | 2.42120 | -1.91010 | 0.69900 |
| H | 2.00450 | -1.58050 | -0.25030 |
| H | 1.66450 | -1.77170 | 1.47150 |
| H | 2.62780 | -2.97790 | 0.61950 |
| C | 4.84660 | -1.74780 | 1.23900 |
| H | 4.88960 | -2.82160 | 1.12130 |
| C | 6.17140 | -1.09570 | 1.59340 |
| H | 6.61460 | -1.67150 | 2.40570 |
| H | 6.01480 | -0.10180 | 2.00890 |

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Compound **5.13**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +200.529083 kJ.

| | | | |
|---|---|---|---|
| H | 3.76730 | -0.42690 | -2.21880 |
| C | 3.75640 | 0.62060 | -1.91330 |
| C | 5.10650 | 2.75530 | -2.55970 |
| C | 2.57390 | 2.76730 | -2.68420 |
| C | 3.87070 | 3.20880 | -3.36600 |
| C | 2.54110 | 1.25890 | -2.57190 |
| C | 5.11340 | 1.21180 | -2.33140 |
| H | 5.00160 | 3.20830 | -1.57180 |
| H | 2.50260 | 3.20370 | -1.68720 |
| H | 3.90000 | 2.79630 | -4.37500 |
| H | 5.45170 | 0.71450 | -3.24000 |
| H | 1.71160 | 3.12700 | -3.24710 |
| H | 3.85890 | 4.29280 | -3.47350 |
| C | 1.53060 | 0.52840 | -3.07200 |
| H | 0.68630 | 0.99520 | -3.55790 |
| H | 1.53070 | -0.54990 | -3.00560 |
| C | 6.44190 | 3.29150 | -3.15510 |
| H | 7.26040 | 2.84830 | -2.58920 |
| C | 6.59190 | 4.81090 | -2.96670 |
| H | 5.86960 | 5.37010 | -3.56100 |
| H | 7.58530 | 5.14490 | -3.26770 |
| H | 6.45760 | 5.09650 | -1.92290 |
| C | 6.67720 | 2.90620 | -4.62780 |
| H | 6.62790 | 1.82920 | -4.78370 |
| H | 7.66490 | 3.22890 | -4.95830 |
| H | 5.94970 | 3.37320 | -5.29170 |
| C | 3.76840 | 0.69190 | -0.37200 |
| H | 3.10710 | 1.47670 | -0.00260 |
| C | 5.98210 | 0.82890 | -1.11460 |
| H | 6.85860 | 1.46700 | -1.01850 |
| O | 5.10250 | 1.07650 | -0.02630 |
| C | 3.40610 | -0.65210 | 0.29780 |
| H | 3.77770 | -1.48520 | -0.29470 |
| H | 2.32360 | -0.78150 | 0.31610 |
| C | 6.47740 | -0.63170 | -1.06380 |
| O | 6.44360 | -1.36570 | -2.05140 |
| C | 7.01950 | -1.15650 | 0.27130 |
| H | 7.93820 | -1.69620 | 0.04260 |
| H | 7.30360 | -0.31590 | 0.90450 |
| C | 3.96280 | -0.76330 | 1.70750 |
| C | 3.15510 | -0.05350 | 2.77690 |
| H | 3.10640 | 1.01490 | 2.56510 |
| H | 3.59630 | -0.18080 | 3.76580 |
| H | 2.13800 | -0.44470 | 2.80830 |
| C | 5.12450 | -1.38510 | 1.99560 |
| H | 5.47400 | -1.36820 | 3.01820 |
| C | 6.05320 | -2.10060 | 1.02180 |
| H | 5.48070 | -2.70720 | 0.31960 |
| H | 6.63550 | -2.81750 | 1.60070 |

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Compound **5.13**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -891.297516289 hartree.
Free Energy: -890.906975 hartree.

| | | | |
|---|---|---|---|
| H | 3.72087 | -0.25845 | -1.44874 |
| C | 3.78180 | 0.83503 | -1.42465 |
| C | 5.15888 | 2.70614 | -2.62633 |
| C | 2.62287 | 2.86653 | -2.45113 |
| C | 3.85301 | 3.08805 | -3.34939 |
| C | 2.53331 | 1.41315 | -2.05134 |
| C | 5.11180 | 1.23691 | -2.13087 |
| H | 5.22408 | 3.34435 | -1.73056 |
| H | 2.71579 | 3.50755 | -1.56098 |
| H | 3.73338 | 2.48381 | -4.25798 |
| H | 5.30628 | 0.55239 | -2.96066 |
| H | 1.70649 | 3.17397 | -2.96753 |
| H | 3.89058 | 4.13693 | -3.66749 |
| C | 1.44921 | 0.67040 | -2.29737 |
| H | 0.55997 | 1.09555 | -2.75693 |
| H | 1.41009 | -0.38956 | -2.05880 |
| C | 6.43420 | 3.00215 | -3.47118 |
| H | 7.28326 | 2.55598 | -2.93303 |
| C | 6.71899 | 4.51076 | -3.56122 |
| H | 5.93777 | 5.04031 | -4.11974 |
| H | 7.66848 | 4.69544 | -4.07727 |
| H | 6.78499 | 4.96578 | -2.56557 |
| C | 6.41808 | 2.37389 | -4.87508 |
| H | 6.22237 | 1.29647 | -4.84646 |
| H | 7.38886 | 2.51708 | -5.36373 |
| H | 5.65936 | 2.83720 | -5.51636 |
| C | 4.01868 | 1.26897 | 0.04819 |
| H | 3.60721 | 2.27261 | 0.22199 |
| C | 6.10955 | 0.97925 | -0.99281 |
| H | 7.01106 | 1.60394 | -1.07513 |
| O | 5.44646 | 1.38573 | 0.20648 |

| | | | |
|---|---|---|---|
| C | 3.41999 | 0.34894 | 1.13421 |
| H | 3.78639 | 0.72375 | 2.09871 |
| H | 2.33637 | 0.52280 | 1.13430 |
| C | 6.61493 | -0.47808 | -0.91911 |
| O | 6.63886 | -1.16923 | -1.92182 |
| C | 7.17367 | -0.99397 | 0.40420 |
| H | 7.57678 | -1.98867 | 0.18811 |
| H | 8.01493 | -0.34954 | 0.69961 |
| C | 3.67819 | -1.14790 | 1.01247 |
| C | 2.46566 | -1.98800 | 0.68170 |
| H | 1.98978 | -1.66160 | -0.25205 |
| H | 1.70042 | -1.89134 | 1.46519 |
| H | 2.71701 | -3.04875 | 0.58349 |
| C | 4.87064 | -1.73165 | 1.21646 |
| H | 4.92679 | -2.81444 | 1.09235 |
| C | 6.16681 | -1.06148 | 1.58496 |
| H | 6.65286 | -1.63323 | 2.38802 |
| H | 5.98967 | -0.05337 | 1.95988 |

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Compound **5.13**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in chloroform was used.

Electronic Energy: -890.928368894 hartree.
Free Energy: -890.532995 hartree.

| | | | |
|---|---|---|---|
| H | 3.74812 | -0.29252 | -1.42726 |
| C | 3.80523 | 0.80290 | -1.42734 |
| C | 5.15821 | 2.66966 | -2.60894 |
| C | 2.63702 | 2.82969 | -2.43329 |
| C | 3.85989 | 3.04845 | -3.33160 |
| C | 2.55721 | 1.37370 | -2.05128 |
| C | 5.12024 | 1.20101 | -2.14277 |
| H | 5.21855 | 3.29360 | -1.70164 |
| H | 2.73672 | 3.46095 | -1.53903 |
| H | 3.74329 | 2.43237 | -4.23269 |
| H | 5.30942 | 0.52959 | -2.98568 |
| H | 1.71806 | 3.13388 | -2.94456 |
| H | 3.90014 | 4.09411 | -3.65811 |
| C | 1.48834 | 0.62285 | -2.32044 |
| H | 0.60070 | 1.04771 | -2.78344 |
| H | 1.46657 | -0.44233 | -2.10407 |
| C | 6.41807 | 2.97026 | -3.45602 |
| H | 7.26713 | 2.47057 | -2.96929 |
| C | 6.73209 | 4.46711 | -3.48173 |
| H | 5.92919 | 5.03491 | -3.96594 |
| H | 7.65331 | 4.66035 | -4.04225 |
| H | 6.86316 | 4.86442 | -2.46927 |
| C | 6.32888 | 2.42716 | -4.88490 |
| H | 6.04022 | 1.37079 | -4.91178 |
| H | 7.29873 | 2.51791 | -5.38548 |
| H | 5.60025 | 2.99126 | -5.47806 |
| C | 4.04822 | 1.27970 | 0.02312 |
| H | 3.64520 | 2.29125 | 0.16467 |
| C | 6.11734 | 0.94697 | -1.01404 |
| H | 7.03829 | 1.53913 | -1.11323 |
| O | 5.46997 | 1.38242 | 0.17446 |
| C | 3.44827 | 0.39168 | 1.12231 |
| H | 3.82494 | 0.76904 | 2.08075 |
| H | 2.36579 | 0.56997 | 1.12253 |
| C | 6.55554 | -0.51749 | -0.88441 |
| O | 6.45373 | -1.28429 | -1.82028 |
| C | 7.17059 | -0.95413 | 0.43356 |
| H | 7.60065 | -1.94435 | 0.25604 |
| H | 7.98421 | -0.26491 | 0.69256 |
| C | 3.69860 | -1.09975 | 0.99144 |
| C | 2.49210 | -1.91579 | 0.60619 |
| H | 2.02944 | -1.52563 | -0.30795 |
| H | 1.72435 | -1.85809 | 1.38874 |
| H | 2.74206 | -2.96845 | 0.44733 |
| C | 4.88110 | -1.68973 | 1.20843 |
| H | 4.94436 | -2.76912 | 1.05930 |
| C | 6.16318 | -1.01595 | 1.60609 |
| H | 6.63932 | -1.58280 | 2.41539 |
| H | 5.97152 | -0.00754 | 1.97286 |

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Compound **5.13**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in chloroform was used.

Electronic Energy: -891.315731614 hartree.
Free Energy: -890.924881 hartree.

| | | | |
|---|---|---|---|
| H | 3.69387 | -0.25051 | -1.45405 |
| C | 3.76658 | 0.84184 | -1.42129 |
| C | 5.15822 | 2.70640 | -2.62772 |
| C | 2.62530 | 2.88945 | -2.43739 |
| C | 3.85226 | 3.10336 | -3.34160 |

| | | | |
|---|---|---|---|
| C | 2.52244 | 1.43524 | -2.04497 |
| C | 5.10071 | 1.23941 | -2.12376 |
| H | 5.23730 | 3.34817 | -1.73609 |
| H | 2.73188 | 3.52173 | -1.54276 |
| H | 3.72161 | 2.50730 | -4.25414 |
| H | 5.29522 | 0.55384 | -2.95257 |
| H | 1.70916 | 3.20978 | -2.94668 |
| H | 3.89826 | 4.15431 | -3.65158 |
| C | 1.43054 | 0.70240 | -2.29192 |
| H | 0.54454 | 1.13790 | -2.75005 |
| H | 1.38060 | -0.35788 | -2.05352 |
| C | 6.43223 | 2.97999 | -3.48322 |
| H | 7.27669 | 2.51574 | -2.95360 |
| C | 6.74634 | 4.48208 | -3.57566 |
| H | 5.97250 | 5.03034 | -4.12711 |
| H | 7.69610 | 4.64712 | -4.09937 |
| H | 6.83213 | 4.93628 | -2.58052 |
| C | 6.39224 | 2.35570 | -4.88782 |
| H | 6.17504 | 1.28158 | -4.86138 |
| H | 7.36318 | 2.47910 | -5.38316 |
| H | 5.63928 | 2.83419 | -5.52533 |
| C | 4.00009 | 1.26327 | 0.05607 |
| H | 3.57986 | 2.26042 | 0.24072 |
| C | 6.09829 | 0.98852 | -0.98258 |
| H | 6.99639 | 1.61762 | -1.06654 |
| O | 5.42930 | 1.39425 | 0.21430 |
| C | 3.40929 | 0.32710 | 1.13231 |
| H | 3.76430 | 0.70077 | 2.10163 |
| H | 2.32368 | 0.48696 | 1.12684 |
| C | 6.62480 | -0.45808 | -0.89824 |
| O | 6.67636 | -1.15162 | -1.90203 |
| C | 7.18172 | -0.96139 | 0.42819 |
| H | 7.60713 | -1.94886 | 0.22071 |
| H | 8.00703 | -0.29820 | 0.72610 |
| C | 3.68689 | -1.16603 | 1.00368 |
| C | 2.49103 | -2.01738 | 0.64473 |
| H | 2.03803 | -1.69695 | -0.30273 |
| H | 1.70311 | -1.92726 | 1.40665 |
| H | 2.75366 | -3.07686 | 0.55462 |
| C | 4.88490 | -1.73654 | 1.21827 |
| H | 4.95830 | -2.81793 | 1.08817 |
| C | 6.16787 | -1.04948 | 1.60119 |
| H | 6.65883 | -1.61823 | 2.40326 |
| H | 5.97244 | -0.04644 | 1.98093 |

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Compound **5.13**
This structure was assigned as incorrect.

B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -891.294537869 hartree.
Free Energy: -890.903946 hartree.

| | | | |
|---|---|---|---|
| H | 3.70764 | -0.20907 | -2.01572 |
| C | 3.76380 | 0.84526 | -1.72698 |
| C | 5.21308 | 2.89744 | -2.51489 |
| C | 2.68096 | 3.04547 | -2.45801 |
| C | 3.95302 | 3.37641 | -3.25678 |
| C | 2.55535 | 1.55090 | -2.30078 |
| C | 5.15551 | 1.37780 | -2.19883 |
| H | 5.21737 | 3.41803 | -1.54432 |
| H | 2.74762 | 3.53105 | -1.47150 |
| H | 3.88178 | 2.89896 | -4.24261 |
| H | 5.48301 | 0.79697 | -3.06596 |
| H | 1.79179 | 3.45148 | -2.95342 |
| H | 4.00916 | 4.45792 | -3.42993 |
| C | 1.46637 | 0.87527 | -2.68204 |
| H | 0.59325 | 1.38215 | -3.08615 |
| H | 1.40634 | -0.20814 | -2.60589 |
| C | 6.53866 | 3.28594 | -3.23408 |
| H | 7.35013 | 2.75924 | -2.71005 |
| C | 6.83796 | 4.78921 | -3.10621 |
| H | 6.09278 | 5.39731 | -3.63308 |
| H | 7.81680 | 5.02883 | -3.53814 |
| H | 6.84774 | 5.10712 | -2.05671 |
| C | 6.60328 | 2.85068 | -4.70811 |
| H | 6.37978 | 1.78600 | -4.83829 |
| H | 7.60716 | 3.02658 | -5.11179 |
| H | 5.89905 | 3.41828 | -5.32739 |
| C | 3.85250 | 0.90460 | -0.16485 |
| H | 3.18840 | 1.66928 | 0.25303 |
| C | 6.01917 | 1.04738 | -0.97239 |
| H | 6.90115 | 1.69484 | -0.88055 |
| O | 5.18765 | 1.33644 | 0.15149 |
| C | 3.53323 | -0.46815 | 0.48049 |
| H | 3.97545 | -1.25714 | -0.13710 |
| H | 2.44405 | -0.60898 | 0.42871 |
| C | 6.50250 | -0.41299 | -0.88101 |
| O | 6.40730 | -1.18438 | -1.81959 |
| C | 7.09415 | -0.86730 | 0.45198 |
| H | 8.01487 | -1.40533 | 0.19619 |
| H | 7.35402 | -0.00981 | 1.07924 |
| C | 4.02599 | -0.59118 | 1.90259 |
| C | 3.17028 | 0.04312 | 2.97069 |

| | | | |
|---|---|---|---|
| H | 3.04412 | 1.12042 | 2.79363 |
| H | 3.60636 | -0.08195 | 3.96680 |
| H | 2.16126 | -0.39240 | 2.98212 |
| C | 5.19171 | -1.18565 | 2.19900 |
| H | 5.50008 | -1.19203 | 3.24503 |
| C | 6.16383 | -1.84282 | 1.24239 |
| H | 5.65084 | -2.48257 | 0.51334 |
| H | 6.80962 | -2.51079 | 1.82283 |

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Compound **5.13**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in chloroform was used.

Electronic Energy: -890.924765491 hartree.
Free Energy: -890.529996 hartree.

| | | | |
|---|---|---|---|
| H | 3.73503 | -0.24710 | -2.03101 |
| C | 3.79079 | 0.81041 | -1.75235 |
| C | 5.21763 | 2.86526 | -2.49806 |
| C | 2.70135 | 3.00947 | -2.43484 |
| C | 3.96401 | 3.34852 | -3.23320 |
| C | 2.58268 | 1.51449 | -2.31548 |
| C | 5.17037 | 1.34806 | -2.22042 |
| H | 5.21825 | 3.36350 | -1.51531 |
| H | 2.78256 | 3.46290 | -1.43548 |
| H | 3.89392 | 2.86979 | -4.21843 |
| H | 5.50674 | 0.79010 | -3.10052 |
| H | 1.80726 | 3.42363 | -2.91181 |
| H | 4.02340 | 4.43023 | -3.40161 |
| C | 1.50144 | 0.83754 | -2.70399 |
| H | 0.62290 | 1.34514 | -3.09527 |
| H | 1.45790 | -0.24776 | -2.64274 |
| C | 6.52843 | 3.26175 | -3.21723 |
| H | 7.34000 | 2.67406 | -2.76490 |
| C | 6.86231 | 4.73813 | -2.99780 |
| H | 6.08896 | 5.38926 | -3.42231 |
| H | 7.81087 | 4.99920 | -3.47975 |
| H | 6.95047 | 4.97229 | -1.93119 |
| C | 6.51437 | 2.94104 | -4.71416 |
| H | 6.21643 | 1.90585 | -4.91484 |
| H | 7.51107 | 3.08794 | -5.14378 |
| H | 5.82414 | 3.59987 | -5.25289 |
| C | 3.87477 | 0.89312 | -0.19919 |
| H | 3.19755 | 1.65301 | 0.20744 |
| C | 6.02623 | 1.01899 | -0.99692 |
| H | 6.92925 | 1.63709 | -0.91261 |
| O | 5.19914 | 1.33574 | 0.11372 |
| C | 3.57241 | -0.47278 | 0.44715 |
| H | 4.04764 | -1.25909 | -0.14895 |
| H | 2.48767 | -0.63352 | 0.37644 |
| C | 6.43916 | -0.45025 | -0.86743 |
| O | 6.25615 | -1.25419 | -1.75908 |
| C | 7.06259 | -0.86821 | 0.45396 |
| H | 7.98694 | -1.39477 | 0.19051 |
| H | 7.32074 | 0.00919 | 1.05276 |
| C | 4.04001 | -0.55066 | 1.87551 |
| C | 3.18065 | 0.14594 | 2.89464 |
| H | 3.06759 | 1.20975 | 2.64847 |
| H | 3.60644 | 0.07616 | 3.89961 |
| H | 2.17030 | -0.28127 | 2.91603 |
| C | 5.19381 | -1.14135 | 2.20604 |
| H | 5.49606 | -1.11176 | 3.25328 |
| C | 6.16082 | -1.83021 | 1.27074 |
| H | 5.64421 | -2.49286 | 0.56562 |
| H | 6.81449 | -2.47197 | 1.86803 |

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Compound **5.13**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in chloroform was used.

Electronic Energy: -891.313252696 hartree.
Free Energy: -890.923367 hartree.

| | | | |
|---|---|---|---|
| H | 3.70921 | -0.21212 | -2.00566 |
| C | 3.76538 | 0.84399 | -1.72337 |
| C | 5.21099 | 2.89878 | -2.50965 |
| C | 2.67667 | 3.03862 | -2.46721 |
| C | 3.95298 | 3.37296 | -3.25798 |
| C | 2.55553 | 1.54455 | -2.30228 |
| C | 5.15585 | 1.37774 | -2.19834 |
| H | 5.20758 | 3.41804 | -1.53863 |
| H | 2.73434 | 3.52819 | -1.48235 |
| H | 3.89046 | 2.89763 | -4.24567 |
| H | 5.47906 | 0.80451 | -3.07176 |
| H | 1.78938 | 3.43800 | -2.97185 |
| H | 4.00551 | 4.45503 | -3.42751 |
| C | 1.46836 | 0.86290 | -2.68167 |
| H | 0.59380 | 1.36534 | -3.09059 |

| | | | |
|---|---|---|---|
| H | 1.40927 | -0.22066 | -2.59625 |
| C | 6.53906 | 3.29837 | -3.21890 |
| H | 7.35277 | 2.79691 | -2.67480 |
| C | 6.80766 | 4.80890 | -3.11441 |
| H | 6.06838 | 5.39513 | -3.67408 |
| H | 7.79489 | 5.05770 | -3.52305 |
| H | 6.78404 | 5.14949 | -2.07160 |
| C | 6.63275 | 2.84120 | -4.68415 |
| H | 6.43627 | 1.76923 | -4.80222 |
| H | 7.63878 | 3.03273 | -5.07728 |
| H | 5.92605 | 3.38201 | -5.32496 |
| C | 3.85378 | 0.90989 | -0.16164 |
| H | 3.20187 | 1.68663 | 0.25252 |
| C | 6.02461 | 1.03762 | -0.97840 |
| H | 6.91058 | 1.67939 | -0.88880 |
| O | 5.19804 | 1.32321 | 0.15138 |
| C | 3.51505 | -0.45391 | 0.49211 |
| H | 3.93437 | -1.25411 | -0.12754 |
| H | 2.42295 | -0.57169 | 0.45500 |
| C | 6.51737 | -0.41876 | -0.89852 |
| O | 6.46003 | -1.17264 | -1.85761 |
| C | 7.09130 | -0.89142 | 0.43333 |
| H | 8.00221 | -1.44673 | 0.17987 |
| H | 7.36946 | -0.04143 | 1.06289 |
| C | 4.02278 | -0.58239 | 1.90902 |
| C | 3.18582 | 0.05808 | 2.98772 |
| H | 3.05571 | 1.13448 | 2.80566 |
| H | 3.63820 | -0.06023 | 3.97812 |
| H | 2.17583 | -0.37495 | 3.01943 |
| C | 5.18921 | -1.18552 | 2.19015 |
| H | 5.51177 | -1.19633 | 3.23225 |
| C | 6.14226 | -1.85224 | 1.22113 |
| H | 5.61029 | -2.47663 | 0.49206 |
| H | 6.77941 | -2.53578 | 1.79248 |

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Compound **5.14**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +81.854645 kJ.

| | | | |
|---|---|---|---|
| H | -1.01710 | -6.68820 | -2.11310 |
| C | -0.10790 | -6.86650 | -1.53730 |
| C | -0.43450 | -6.78260 | -0.03120 |
| H | 0.19670 | -7.88720 | -1.77250 |
| C | 0.80170 | -6.89400 | 0.85360 |
| C | 1.46060 | -5.89430 | 1.47880 |
| C | 1.04840 | -4.48070 | 1.43060 |
| C | 1.88790 | -3.49600 | -1.66180 |
| H | 2.53360 | -3.61190 | -2.53330 |
| C | 0.66000 | -4.40950 | -1.84970 |
| H | -0.03720 | -4.24220 | -1.03250 |
| C | 1.00150 | -5.90590 | -2.01210 |
| H | 0.11120 | -4.08690 | -2.73540 |
| H | 1.92170 | -6.15750 | -1.48970 |
| H | 1.21960 | -6.10060 | -3.06290 |
| O | -0.07850 | -4.11260 | 1.76270 |
| H | -0.98960 | -5.86990 | 0.17920 |
| H | -1.11560 | -7.59020 | 0.23920 |
| H | 2.35600 | -6.11810 | 2.03780 |
| C | 2.74390 | -3.72360 | -0.38680 |
| C | 2.09730 | -3.43660 | 0.99700 |
| H | 3.61890 | -3.07810 | -0.47000 |
| H | 3.16160 | -4.72950 | -0.39300 |
| C | 1.57640 | -1.98900 | 1.10560 |
| H | 2.89470 | -3.53140 | 1.73420 |
| H | 1.20880 | -7.89100 | 0.93520 |
| H | 1.55810 | -2.45710 | -1.69040 |
| H | 1.24310 | -1.76700 | 2.12030 |
| H | 0.72800 | -1.81750 | 0.44220 |
| H | 2.35330 | -1.26840 | 0.85150 |

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Compound **5.14**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +83.382271 kJ.

| | | | |
|---|---|---|---|
| H | -0.91680 | -7.29350 | -1.78410 |
| C | 0.10300 | -7.05090 | -1.48250 |
| C | 0.19820 | -7.13930 | 0.05570 |
| H | 0.73480 | -7.82120 | -1.92680 |
| C | -0.55790 | -6.02120 | 0.76340 |
| C | -0.04400 | -4.90280 | 1.31930 |
| C | 1.39640 | -4.59130 | 1.36270 |
| C | 2.15210 | -3.72300 | -1.77140 |
| H | 3.22280 | -3.52900 | -1.69420 |
| C | 1.93350 | -5.24850 | -1.82490 |
| H | 2.55140 | -5.66660 | -2.62060 |
| C | 0.47150 | -5.67490 | -2.07430 |
| H | 2.33320 | -5.69740 | -0.91910 |

| | | | |
|---|---|---|---|
| H | 0.29060 | -5.68590 | -3.14980 |
| H | -0.22510 | -4.93520 | -1.68620 |
| O | 2.22500 | -5.35050 | 1.86140 |
| H | -0.21570 | -8.09050 | 0.39200 |
| H | 1.24170 | -7.16600 | 0.36510 |
| H | -0.71060 | -4.17070 | 1.74770 |
| C | 1.42700 | -2.94620 | -0.64260 |
| C | 1.87920 | -3.23900 | 0.81280 |
| H | 0.34650 | -3.05110 | -0.73220 |
| H | 1.60890 | -1.88810 | -0.83470 |
| C | 1.47280 | -2.10380 | 1.76970 |
| H | 2.96900 | -3.28300 | 0.81600 |
| H | -1.63190 | -6.13390 | 0.76480 |
| H | 1.84970 | -3.30070 | -2.73070 |
| H | 1.74440 | -2.33750 | 2.80040 |
| H | 0.39920 | -1.91570 | 1.74050 |
| H | 1.97900 | -1.17480 | 1.50700 |

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Compound **5.14**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -504.994404145 hartree.
Free Energy: -504.756416 hartree.

| | | | |
|---|---|---|---|
| H | -1.04236 | -6.64093 | -2.08263 |
| C | -0.11946 | -6.84059 | -1.52388 |
| C | -0.43895 | -6.75108 | -0.01456 |
| H | 0.17863 | -7.86822 | -1.76671 |
| C | 0.81021 | -6.88388 | 0.80797 |
| C | 1.48012 | -5.88761 | 1.39918 |
| C | 1.03226 | -4.46163 | 1.38702 |
| C | 1.93799 | -3.52608 | -1.62212 |
| H | 2.58636 | -3.70701 | -2.49028 |
| C | 0.68211 | -4.39704 | -1.74850 |
| H | 0.06215 | -4.26098 | -0.85604 |
| C | 0.98881 | -5.88493 | -1.97789 |
| H | 0.07301 | -4.02752 | -2.58286 |
| H | 1.91325 | -6.15710 | -1.45570 |
| H | 1.18697 | -6.04680 | -3.04454 |
| O | -0.10453 | -4.14047 | 1.68270 |
| H | -0.94499 | -5.81255 | 0.21671 |
| H | -1.13343 | -7.55902 | 0.24362 |
| H | 2.45147 | -6.08330 | 1.85194 |
| C | 2.77384 | -3.75506 | -0.35410 |
| C | 2.08149 | -3.42706 | 0.99023 |
| H | 3.66640 | -3.12100 | -0.41874 |
| H | 3.13877 | -4.78856 | -0.32645 |
| C | 1.50280 | -2.01836 | 1.03424 |
| H | 2.86601 | -3.51580 | 1.75854 |
| H | 1.26219 | -7.87701 | 0.82466 |
| H | 1.65143 | -2.46872 | -1.67316 |
| H | 1.14905 | -1.77054 | 2.03838 |
| H | 0.64957 | -1.92066 | 0.35638 |
| H | 2.26142 | -1.28446 | 0.74277 |

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Compound **5.14**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -505.229970215 hartree.
Free Energy: -504.994763 hartree.

| | | | |
|---|---|---|---|
| H | -1.02562 | -6.73602 | -2.09702 |
| C | -0.09698 | -6.89192 | -1.53113 |
| C | -0.43964 | -6.79200 | -0.01873 |
| H | 0.23381 | -7.91513 | -1.75574 |
| C | 0.78462 | -6.88470 | 0.85011 |
| C | 1.43275 | -5.86519 | 1.43886 |
| C | 1.00749 | -4.43293 | 1.37932 |
| C | 1.88773 | -3.50361 | -1.64824 |
| H | 2.55339 | -3.63159 | -2.51446 |
| C | 0.65756 | -4.41589 | -1.82712 |
| H | -0.01675 | -4.27343 | -0.97749 |
| C | 0.98993 | -5.91309 | -2.01089 |
| H | 0.09303 | -4.06619 | -2.70227 |
| H | 1.91900 | -6.15460 | -1.48200 |
| H | 1.19401 | -6.10837 | -3.07243 |
| O | -0.14314 | -4.08488 | 1.61767 |
| H | -0.97601 | -5.86480 | 0.18855 |
| H | -1.12345 | -7.61440 | 0.23073 |
| H | 2.38747 | -6.05709 | 1.92855 |
| C | 2.74327 | -3.72370 | -0.38209 |
| C | 2.09346 | -3.41941 | 1.00162 |
| H | 3.62634 | -3.07593 | -0.46235 |
| H | 3.12876 | -4.74992 | -0.37034 |
| C | 1.59308 | -1.97880 | 1.13219 |

| | | | |
|---|---|---|---|
| H | 2.90136 | -3.57569 | 1.73473 |
| H | 1.24116 | -7.87385 | 0.92004 |
| H | 1.55669 | -2.45737 | -1.68047 |
| H | 1.26202 | -1.76781 | 2.15419 |
| H | 0.74364 | -1.78259 | 0.47120 |
| H | 2.39361 | -1.27310 | 0.88121 |

---

Compound **5.14**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -505.216797159 hartree.
Free Energy: -504.981174 hartree.

| | | | |
|---|---|---|---|
| H | -1.02711 | -6.72947 | -2.09249 |
| C | -0.09930 | -6.88922 | -1.52648 |
| C | -0.44137 | -6.79243 | -0.01310 |
| H | 0.22809 | -7.91279 | -1.75550 |
| C | 0.78439 | -6.88790 | 0.85412 |
| C | 1.43458 | -5.86696 | 1.43668 |
| C | 1.00831 | -4.43476 | 1.36421 |
| C | 1.88644 | -3.50020 | -1.64842 |
| H | 2.54999 | -3.62324 | -2.51670 |
| C | 0.65693 | -4.41421 | -1.82712 |
| H | -0.02117 | -4.26671 | -0.98202 |
| C | 0.99074 | -5.91223 | -2.00370 |
| H | 0.09774 | -4.06860 | -2.70710 |
| H | 1.91636 | -6.15261 | -1.46830 |
| H | 1.20184 | -6.11153 | -3.06291 |
| O | -0.14737 | -4.08744 | 1.56284 |
| H | -0.97531 | -5.86602 | 0.20189 |
| H | -1.12584 | -7.61442 | 0.23559 |
| H | 2.38845 | -6.05780 | 1.92831 |
| C | 2.74725 | -3.72019 | -0.38507 |
| C | 2.10021 | -3.42018 | 1.00075 |
| H | 3.62903 | -3.07080 | -0.46821 |
| H | 3.13452 | -4.74601 | -0.37619 |
| C | 1.59442 | -1.98153 | 1.13660 |
| H | 2.90834 | -3.57888 | 1.73364 |
| H | 1.23843 | -7.87808 | 0.92777 |
| H | 1.55234 | -2.45511 | -1.67643 |
| H | 1.25497 | -1.78145 | 2.15729 |
| H | 0.74484 | -1.79244 | 0.47476 |
| H | 2.39187 | -1.27079 | 0.89152 |

---

Compound **5.14**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -504.992489739 hartree.
Free Energy: -504.755155 hartree.

| | | | |
|---|---|---|---|
| H | -0.93306 | -7.28086 | -1.76034 |
| C | 0.09727 | -7.04254 | -1.46813 |
| C | 0.21765 | -7.12791 | 0.07057 |
| H | 0.73681 | -7.81930 | -1.90593 |
| C | -0.53874 | -6.01080 | 0.72861 |
| C | -0.01838 | -4.88909 | 1.24114 |
| C | 1.44827 | -4.60548 | 1.30838 |
| C | 2.11549 | -3.71578 | -1.76757 |
| H | 3.19101 | -3.49989 | -1.72537 |
| C | 1.91264 | -5.23521 | -1.74600 |
| H | 2.57985 | -5.69442 | -2.48623 |
| C | 0.47003 | -5.67011 | -2.03896 |
| H | 2.24570 | -5.62369 | -0.77834 |
| H | 0.31233 | -5.67691 | -3.12451 |
| H | -0.22906 | -4.92791 | -1.63698 |
| O | 2.23808 | -5.40709 | 1.77422 |
| H | -0.19113 | -8.09003 | 0.40025 |
| H | 1.26511 | -7.10735 | 0.37622 |
| H | -0.68559 | -4.09037 | 1.56197 |
| C | 1.42545 | -2.93611 | -0.63953 |
| C | 1.91962 | -3.25260 | 0.78367 |
| H | 0.33725 | -3.07601 | -0.68024 |
| H | 1.59689 | -1.86639 | -0.81423 |
| C | 1.47427 | -2.15819 | 1.76618 |
| H | 3.01535 | -3.30474 | 0.78800 |
| H | -1.62649 | -6.08216 | 0.67651 |
| H | 1.75910 | -3.32090 | -2.72868 |
| H | 1.76527 | -2.39842 | 2.79391 |
| H | 0.38827 | -2.01709 | 1.74026 |
| H | 1.93863 | -1.20486 | 1.49558 |

---

Compound **5.14**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -505.229236689 hartree.
Free Energy: -504.994783 hartree.

| | | | |
|---|---|---|---|
| H | -0.95392 | -7.27278 | -1.76681 |
| C | 0.08079 | -7.04939 | -1.47302 |
| C | 0.19843 | -7.14260 | 0.07391 |
| H | 0.70409 | -7.84343 | -1.90674 |
| C | -0.54177 | -6.02950 | 0.76296 |
| C | -0.01208 | -4.90877 | 1.28251 |
| C | 1.45062 | -4.60240 | 1.32910 |
| C | 2.14286 | -3.71922 | -1.76687 |
| H | 3.22258 | -3.52135 | -1.70937 |
| C | 1.92758 | -5.24506 | -1.79577 |
| H | 2.57769 | -5.67116 | -2.57214 |
| C | 0.47215 | -5.68264 | -2.06392 |
| H | 2.28990 | -5.67140 | -0.85532 |
| H | 0.29608 | -5.70400 | -3.14800 |
| H | -0.21880 | -4.93060 | -1.66604 |
| O | 2.26638 | -5.40675 | 1.76502 |
| H | -0.21899 | -8.10756 | 0.39091 |
| H | 1.24732 | -7.13997 | 0.37587 |
| H | -0.68221 | -4.12003 | 1.62183 |
| C | 1.44495 | -2.93130 | -0.63796 |
| C | 1.90776 | -3.23333 | 0.80935 |
| H | 0.35619 | -3.05482 | -0.70146 |
| H | 1.63222 | -1.86417 | -0.81950 |
| C | 1.44731 | -2.12123 | 1.77566 |
| H | 3.00401 | -3.27284 | 0.83422 |
| H | -1.63085 | -6.10036 | 0.73638 |
| H | 1.80910 | -3.29407 | -2.72484 |
| H | 1.74229 | -2.34027 | 2.80859 |
| H | 0.35988 | -1.98379 | 1.75429 |
| H | 1.90635 | -1.16735 | 1.49156 |

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Compound **5.14**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -505.215720598 hartree.
Free Energy: -504.980562 hartree.

| | | | |
|---|---|---|---|
| H | -0.96125 | -7.26285 | -1.76399 |
| C | 0.07421 | -7.04342 | -1.46916 |
| C | 0.19432 | -7.14174 | 0.07779 |
| H | 0.69370 | -7.83829 | -1.90641 |
| C | -0.53924 | -6.02818 | 0.77420 |
| C | -0.00013 | -4.91075 | 1.28971 |
| C | 1.46522 | -4.60929 | 1.31009 |
| C | 2.15733 | -3.72470 | -1.76390 |
| H | 3.23808 | -3.53670 | -1.69755 |
| C | 1.93004 | -5.24947 | -1.79588 |
| H | 2.57183 | -5.67561 | -2.57885 |
| C | 0.46983 | -5.67650 | -2.05732 |
| H | 2.29592 | -5.68116 | -0.86020 |
| H | 0.28599 | -5.69195 | -3.14000 |
| H | -0.21490 | -4.92284 | -1.65178 |
| O | 2.29123 | -5.42896 | 1.68681 |
| H | -0.22589 | -8.10606 | 0.39321 |
| H | 1.24187 | -7.14267 | 0.38244 |
| H | -0.66342 | -4.12283 | 1.64349 |
| C | 1.45763 | -2.92914 | -0.64079 |
| C | 1.90919 | -3.22682 | 0.81141 |
| H | 0.36843 | -3.04856 | -0.70905 |
| H | 1.64855 | -1.86304 | -0.82647 |
| C | 1.42153 | -2.12247 | 1.77231 |
| H | 3.00537 | -3.25508 | 0.84786 |
| H | -1.62884 | -6.09729 | 0.76131 |
| H | 1.83549 | -3.29555 | -2.72390 |
| H | 1.70773 | -2.33726 | 2.80796 |
| H | 0.33231 | -2.00273 | 1.73742 |
| H | 1.86578 | -1.16029 | 1.49367 |

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Compound **5.15**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +83.497330 kJ.

| | | | |
|---|---|---|---|
| H | 5.18570 | -5.45000 | -8.42320 |
| C | 5.11570 | -5.00000 | -9.41450 |
| C | 6.36490 | -5.43460 | -10.21190 |
| H | 4.22150 | -5.43470 | -9.86360 |
| C | 6.33300 | -4.88820 | -11.61930 |
| C | 7.28120 | -4.09680 | -12.15010 |
| C | 7.02310 | -3.30600 | -13.36210 |
| C | 5.44850 | -1.72630 | -11.07490 |
| H | 5.32960 | -0.77040 | -10.56290 |
| C | 4.41230 | -2.71090 | -10.48780 |
| H | 3.51770 | -2.14330 | -10.22720 |

| | | | |
|---|---|---|---|
| C | 4.91320 | -3.47380 | -9.23480 |
| H | 4.06840 | -3.41810 | -11.24050 |
| H | 4.16560 | -3.33860 | -8.45180 |
| H | 5.82040 | -3.02060 | -8.83320 |
| O | 7.90700 | -3.09300 | -14.18980 |
| H | 8.19230 | -3.88280 | -11.61230 |
| C | 5.33870 | -1.48260 | -12.60100 |
| C | 5.61780 | -2.68210 | -13.55420 |
| H | 6.02360 | -0.67400 | -12.86220 |
| H | 4.34170 | -1.09380 | -12.81090 |
| C | 5.38510 | -2.26230 | -15.01910 |
| H | 4.88310 | -3.45670 | -13.34740 |
| H | 6.46190 | -2.03150 | -10.82130 |
| H | 5.57960 | -3.08920 | -15.70350 |
| H | 6.03910 | -1.43770 | -15.30650 |
| H | 4.35570 | -1.94200 | -15.17860 |
| H | 7.27280 | -5.10810 | -9.70270 |
| H | 6.40770 | -6.52330 | -10.26430 |
| H | 5.41610 | -5.08030 | -12.15610 |

---

Compound **5.15**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +90.198425 kJ.

| | | | |
|---|---|---|---|
| H | 6.73530 | -4.10920 | -8.68440 |
| C | 5.88470 | -4.66440 | -9.08260 |
| C | 6.34570 | -5.62120 | -10.20660 |
| H | 5.52500 | -5.27810 | -8.25540 |
| C | 6.92710 | -4.85680 | -11.37390 |
| C | 6.20050 | -4.50870 | -12.44800 |
| C | 6.67170 | -3.45680 | -13.35180 |
| C | 4.37700 | -2.08470 | -11.50400 |
| H | 3.84310 | -2.96040 | -11.87260 |
| C | 5.21970 | -2.41840 | -10.24880 |
| H | 6.27100 | -2.50400 | -10.51650 |
| C | 4.75320 | -3.68490 | -9.48480 |
| H | 5.20140 | -1.56360 | -9.57130 |
| H | 4.00040 | -4.23470 | -10.05010 |
| H | 4.23890 | -3.35770 | -8.58010 |
| O | 7.84720 | -3.35280 | -13.70250 |
| H | 5.18090 | -4.84520 | -12.55400 |
| C | 5.17840 | -1.45560 | -12.67210 |
| C | 5.62300 | -2.42320 | -13.80870 |
| H | 6.03780 | -0.90290 | -12.28860 |
| H | 4.53840 | -0.69750 | -13.12530 |
| C | 6.11230 | -1.62890 | -15.03590 |
| H | 4.75010 | -2.99330 | -14.12690 |
| H | 3.59120 | -1.39200 | -11.19870 |
| H | 6.44370 | -2.29520 | -15.83360 |
| H | 6.95130 | -0.98020 | -14.78020 |
| H | 5.31880 | -1.00280 | -15.44350 |
| H | 7.10100 | -6.31280 | -9.83150 |
| H | 5.50630 | -6.23050 | -10.54480 |
| H | 7.91200 | -4.43180 | -11.23000 |

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Compound **5.15**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -504.988213075 hartree.
Free Energy: -504.750368 hartree.

| | | | |
|---|---|---|---|
| H | 5.22659 | -5.42988 | -8.37460 |
| C | 5.12271 | -4.99475 | -9.37517 |
| C | 6.25193 | -5.57560 | -10.25835 |
| H | 4.15063 | -5.32961 | -9.76087 |
| C | 6.22983 | -4.91813 | -11.60045 |
| C | 7.15547 | -4.05860 | -12.03898 |
| C | 6.98438 | -3.14025 | -13.19609 |
| C | 5.38098 | -1.65594 | -11.14261 |
| H | 5.18656 | -0.68923 | -10.66289 |
| C | 4.49273 | -2.73583 | -10.49595 |
| H | 3.54564 | -2.27601 | -10.18980 |
| C | 5.13147 | -3.45930 | -9.28242 |
| H | 4.21283 | -3.47718 | -11.25090 |
| H | 4.61167 | -3.16446 | -8.36472 |
| H | 6.17088 | -3.12555 | -9.15844 |
| O | 7.95641 | -2.65062 | -13.74494 |
| H | 8.08638 | -3.92531 | -11.48780 |
| C | 5.19025 | -1.48392 | -12.65595 |
| C | 5.57101 | -2.69030 | -13.55553 |
| H | 5.79310 | -0.62894 | -12.98869 |
| H | 4.14307 | -1.23296 | -12.87045 |
| C | 5.48146 | -2.29735 | -15.02663 |
| H | 4.86883 | -3.50583 | -13.35598 |
| H | 6.43541 | -1.87503 | -10.93837 |

| | | | |
|---|---|---|---|
| H | 5.68645 | -3.15070 | -15.68071 |
| H | 6.21191 | -1.51661 | -15.25613 |
| H | 4.48175 | -1.91894 | -15.26301 |
| H | 7.21967 | -5.39736 | -9.77520 |
| H | 6.11346 | -6.65991 | -10.34589 |
| H | 5.32956 | -5.08761 | -12.19020 |

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Compound **5.15**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -505.226118557 hartree.
Free Energy: -504.991722 hartree.

| | | | |
|---|---|---|---|
| H | 5.25271 | -5.44101 | -8.37132 |
| C | 5.13412 | -4.99870 | -9.36917 |
| C | 6.30645 | -5.52116 | -10.24563 |
| H | 4.18912 | -5.39431 | -9.76791 |
| C | 6.26488 | -4.89640 | -11.60374 |
| C | 7.20726 | -4.09098 | -12.11976 |
| C | 7.01717 | -3.18026 | -13.27557 |
| C | 5.40590 | -1.69226 | -11.12226 |
| H | 5.26563 | -0.71414 | -10.64252 |
| C | 4.44204 | -2.71329 | -10.46948 |
| H | 3.52482 | -2.18433 | -10.17970 |
| C | 5.01348 | -3.46411 | -9.22858 |
| H | 4.11598 | -3.44756 | -11.21322 |
| H | 4.36752 | -3.27022 | -8.36308 |
| H | 5.99536 | -3.04944 | -8.96088 |
| O | 7.98765 | -2.71876 | -13.86911 |
| H | 8.17396 | -3.99301 | -11.62524 |
| C | 5.24616 | -1.49223 | -12.64359 |
| C | 5.59556 | -2.69226 | -13.58109 |
| H | 5.87998 | -0.64718 | -12.94572 |
| H | 4.21164 | -1.19698 | -12.86786 |
| C | 5.44885 | -2.28247 | -15.05004 |
| H | 4.88858 | -3.50184 | -13.37046 |
| H | 6.44148 | -1.97459 | -10.90509 |
| H | 5.62157 | -3.13307 | -15.71981 |
| H | 6.17079 | -1.50297 | -15.31253 |
| H | 4.44006 | -1.89985 | -15.24426 |
| H | 7.26459 | -5.30094 | -9.75881 |
| H | 6.21580 | -6.61497 | -10.31266 |
| H | 5.33389 | -5.04242 | -12.14864 |

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Compound **5.15**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -505.211736240 hartree.
Free Energy: -504.977314 hartree.

| | | | |
|---|---|---|---|
| H | 5.24632 | -5.44264 | -8.36869 |
| C | 5.13335 | -5.00058 | -9.36720 |
| C | 6.30346 | -5.52790 | -10.24362 |
| H | 4.18573 | -5.39039 | -9.76585 |
| C | 6.26568 | -4.90102 | -11.60223 |
| C | 7.20337 | -4.08999 | -12.11437 |
| C | 7.01297 | -3.17546 | -13.27126 |
| C | 5.39996 | -1.68933 | -11.12549 |
| H | 5.25801 | -0.71179 | -10.64575 |
| C | 4.44330 | -2.71439 | -10.46818 |
| H | 3.52454 | -2.19131 | -10.17365 |
| C | 5.02499 | -3.46435 | -9.23107 |
| H | 4.11707 | -3.44888 | -11.21147 |
| H | 4.39459 | -3.25979 | -8.35703 |
| H | 6.01434 | -3.05717 | -8.98132 |
| O | 7.98027 | -2.70578 | -13.85583 |
| H | 8.17056 | -3.98793 | -11.62228 |
| C | 5.23463 | -1.49322 | -12.64693 |
| C | 5.58853 | -2.69250 | -13.58229 |
| H | 5.86624 | -0.64856 | -12.95310 |
| H | 4.19885 | -1.20042 | -12.86903 |
| C | 5.45544 | -2.28037 | -15.05266 |
| H | 4.88056 | -3.50391 | -13.37754 |
| H | 6.43713 | -1.96808 | -10.91200 |
| H | 5.62136 | -3.13343 | -15.71974 |
| H | 6.19666 | -1.51647 | -15.30378 |
| H | 4.45506 | -1.88040 | -15.25319 |
| H | 7.26150 | -5.30833 | -9.75603 |
| H | 6.21423 | -6.62196 | -10.30856 |
| H | 5.33431 | -5.04533 | -12.14757 |

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Compound **5.15**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -504.987854592 hartree.
Free Energy: -504.750911 hartree.

| | | | |
|---|---|---|---|
| H | 6.35680 | -3.88669 | -8.96410 |
| C | 5.58146 | -4.58716 | -9.30334 |
| C | 6.22726 | -5.60160 | -10.27891 |
| H | 5.25328 | -5.13112 | -8.41124 |
| C | 6.96415 | -4.83010 | -11.32470 |
| C | 6.46945 | -4.46057 | -12.50934 |
| C | 7.08540 | -3.27954 | -13.17683 |
| C | 5.51922 | -1.76847 | -11.06750 |
| H | 5.67811 | -0.69453 | -10.91472 |
| C | 4.54903 | -2.28330 | -9.99366 |
| H | 4.86682 | -1.90995 | -9.01138 |
| C | 4.38942 | -3.81100 | -9.90886 |
| H | 3.56123 | -1.84091 | -10.18286 |
| H | 4.16792 | -4.21088 | -10.90632 |
| H | 3.49731 | -4.01763 | -9.30735 |
| O | 8.28929 | -3.14424 | -13.28101 |
| H | 5.50125 | -4.82002 | -12.85360 |
| C | 5.00584 | -2.01213 | -12.49850 |
| C | 6.10653 | -2.17083 | -13.57061 |
| H | 4.35593 | -1.17994 | -12.79642 |
| H | 4.36934 | -2.90260 | -12.51368 |
| C | 6.85357 | -0.87022 | -13.84426 |
| H | 5.61541 | -2.50728 | -14.49682 |
| H | 6.50044 | -2.23825 | -10.92269 |
| H | 7.61127 | -1.00472 | -14.61981 |
| H | 7.36535 | -0.51838 | -12.94219 |
| H | 6.15487 | -0.09284 | -14.16906 |
| H | 6.91134 | -6.25501 | -9.72669 |
| H | 5.44628 | -6.22723 | -10.72640 |
| H | 7.90443 | -4.37507 | -11.00776 |

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Compound **5.15**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -505.224489649 hartree.
Free Energy: -504.991282 hartree.

| | | | |
|---|---|---|---|
| H | 6.78096 | -4.16194 | -8.70248 |
| C | 5.88467 | -4.67752 | -9.07447 |
| C | 6.28530 | -5.63103 | -10.23644 |
| H | 5.52915 | -5.30768 | -8.24846 |
| C | 6.87769 | -4.86962 | -11.38031 |
| C | 6.21558 | -4.51330 | -12.49174 |
| C | 6.70577 | -3.38246 | -13.32026 |
| C | 4.38993 | -2.12807 | -11.51064 |
| H | 3.91909 | -3.05729 | -11.85468 |
| C | 5.25776 | -2.41554 | -10.25918 |
| H | 6.29855 | -2.55445 | -10.56247 |
| C | 4.79326 | -3.63963 | -9.41688 |
| H | 5.26471 | -1.51910 | -9.62514 |
| H | 3.97511 | -4.15805 | -9.93635 |
| H | 4.36020 | -3.28729 | -8.47222 |
| O | 7.89829 | -3.15133 | -13.48715 |
| H | 5.20030 | -4.86545 | -12.66314 |
| C | 5.12708 | -1.47186 | -12.70565 |
| C | 5.62235 | -2.42839 | -13.83816 |
| H | 5.98086 | -0.88097 | -12.34589 |
| H | 4.45104 | -0.75786 | -13.19262 |
| C | 6.12403 | -1.62494 | -15.04232 |
| H | 4.75908 | -3.03727 | -14.14252 |
| H | 3.55594 | -1.47916 | -11.21344 |
| H | 6.45185 | -2.28505 | -15.85338 |
| H | 6.97547 | -0.99479 | -14.76619 |
| H | 5.32839 | -0.97894 | -15.43108 |
| H | 7.00827 | -6.36083 | -9.84733 |
| H | 5.39841 | -6.18751 | -10.56579 |
| H | 7.86801 | -4.44099 | -11.22078 |

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Compound **5.15**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -505.210561202 hartree.
Free Energy: -504.976414 hartree.

| | | | |
|---|---|---|---|
| H | 6.78329 | -4.14837 | -8.71056 |
| C | 5.89198 | -4.67581 | -9.07782 |
| C | 6.30072 | -5.63857 | -10.23006 |
| H | 5.54031 | -5.29771 | -8.24422 |
| C | 6.88285 | -4.88016 | -11.38180 |
| C | 6.20716 | -4.51508 | -12.48088 |
| C | 6.69568 | -3.37654 | -13.30370 |
| C | 4.38159 | -2.10771 | -11.50830 |

| | | | |
|---|---|---|---|
| H | 3.88930 | -3.02649 | -11.85149 |
| C | 5.25826 | -2.41792 | -10.26743 |
| H | 6.29468 | -2.55837 | -10.58282 |
| C | 4.79319 | -3.65131 | -9.43905 |
| H | 5.27616 | -1.53150 | -9.61998 |
| H | 3.99522 | -4.17998 | -9.97901 |
| H | 4.33200 | -3.30888 | -8.50431 |
| O | 7.88514 | -3.12961 | -13.44560 |
| H | 5.18974 | -4.86619 | -12.64319 |
| C | 5.11823 | -1.46114 | -12.70900 |
| C | 5.61212 | -2.42643 | -13.83327 |
| H | 5.97427 | -0.87045 | -12.35485 |
| H | 4.44247 | -0.74901 | -13.19916 |
| C | 6.12787 | -1.63332 | -15.03934 |
| H | 4.74687 | -3.03370 | -14.13804 |
| H | 3.56265 | -1.44522 | -11.20023 |
| H | 6.43104 | -2.30183 | -15.85205 |
| H | 7.00304 | -1.03862 | -14.76216 |
| H | 5.35109 | -0.96053 | -15.41967 |
| H | 7.02723 | -6.36179 | -9.83565 |
| H | 5.41675 | -6.20395 | -10.55259 |
| H | 7.87620 | -4.45209 | -11.24096 |

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Compound **5.16**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -126.481628 kJ.

| | | | |
|---|---|---|---|
| C | 0.31640 | -6.55660 | 2.17300 |
| H | 1.05880 | -7.31940 | 2.35590 |
| C | 0.68080 | -5.27120 | 2.37880 |
| H | 1.68390 | -5.04350 | 2.70590 |
| C | -0.23130 | -4.12840 | 2.22930 |
| C | -0.57590 | -3.32910 | 3.50530 |
| H | -0.36270 | -3.98120 | 4.35220 |
| C | -2.06250 | -2.88240 | 3.62650 |
| H | -2.42150 | -2.51580 | 2.66510 |
| H | -2.08890 | -2.02590 | 4.29900 |
| C | -3.04840 | -3.96310 | 4.15620 |
| H | -2.78120 | -4.17740 | 5.19240 |
| C | -2.85520 | -5.23720 | 3.35850 |
| H | -2.98650 | -5.12580 | 2.29130 |
| C | -2.39150 | -6.39680 | 3.85430 |
| H | -2.22790 | -6.47350 | 4.91990 |
| C | -1.86720 | -7.45060 | 3.00490 |
| C | -1.97170 | -8.72740 | 3.40720 |
| H | -1.53980 | -9.53450 | 2.83360 |
| H | -2.49560 | -8.99020 | 4.31500 |
| C | -1.05220 | -7.09580 | 1.76500 |
| H | -1.58620 | -6.37790 | 1.14300 |
| H | -0.90890 | -7.97500 | 1.13560 |
| C | -4.52940 | -3.50140 | 4.12740 |
| H | -4.80220 | -3.30020 | 3.08970 |
| C | -5.48410 | -4.59300 | 4.64740 |
| H | -6.51960 | -4.25180 | 4.63030 |
| H | -5.24510 | -4.87310 | 5.67370 |
| H | -5.44070 | -5.49610 | 4.03820 |
| C | -4.76000 | -2.20310 | 4.92170 |
| H | -5.81740 | -1.93750 | 4.94210 |
| H | -4.23670 | -1.35640 | 4.47820 |
| H | -4.42510 | -2.30310 | 5.95470 |
| O | -0.71690 | -3.80260 | 1.14590 |
| O | 0.31200 | -2.22350 | 3.65220 |
| Si | 0.63720 | -0.96980 | 2.55400 |
| C | 1.92820 | -1.56230 | 1.31120 |
| H | 1.52560 | -2.32530 | 0.64640 |
| H | 2.79740 | -1.98480 | 1.81240 |
| H | 2.27690 | -0.74410 | 0.68340 |
| C | -0.93250 | -0.39040 | 1.68290 |
| H | -1.34060 | -1.16940 | 1.04000 |
| H | -1.70520 | -0.10860 | 2.39620 |
| H | -0.73850 | 0.47510 | 1.05190 |
| C | 1.36340 | 0.46420 | 3.58530 |
| C | 2.63520 | -0.02610 | 4.29830 |
| H | 3.40020 | -0.33350 | 3.58460 |
| H | 2.42270 | -0.88380 | 4.93830 |
| H | 3.06700 | 0.75390 | 4.92580 |
| C | 1.70530 | 1.64830 | 2.66440 |
| H | 2.43880 | 1.36780 | 1.90800 |
| H | 2.12220 | 2.48230 | 3.22960 |
| H | 0.82160 | 2.01740 | 2.14310 |
| C | 0.32180 | 0.89970 | 4.63020 |
| H | 0.04310 | 0.06810 | 5.27940 |
| H | -0.59110 | 1.26270 | 4.15700 |
| H | 0.70280 | 1.70000 | 5.26490 |

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Compound **5.16**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.

Energy: -118.390511 kJ.

| | | | |
|---|---|---|---|
| C | -0.62850 | -5.75930 | 1.11590 |
| H | -0.89430 | -5.85450 | 0.07360 |
| C | -0.41410 | -4.50760 | 1.58710 |
| H | -0.50720 | -3.66700 | 0.91620 |
| C | -0.09720 | -4.17720 | 2.99090 |
| C | -0.77490 | -2.95050 | 3.63410 |
| H | -0.47320 | -2.93250 | 4.68180 |
| C | -2.32840 | -2.90260 | 3.58280 |
| H | -2.65340 | -2.80970 | 2.54590 |
| H | -2.62290 | -1.96590 | 4.05670 |
| C | -3.09660 | -4.06080 | 4.27890 |
| H | -2.56540 | -4.29030 | 5.20460 |
| C | -3.05720 | -5.29120 | 3.39400 |
| H | -3.51490 | -5.19310 | 2.41990 |
| C | -2.30120 | -6.36940 | 3.64690 |
| H | -1.76600 | -6.43790 | 4.58380 |
| C | -1.95680 | -7.29480 | 2.59380 |
| C | -2.81920 | -8.25270 | 2.21810 |
| H | -2.58780 | -8.93330 | 1.41200 |
| H | -3.77230 | -8.37210 | 2.71320 |
| C | -0.62730 | -7.08180 | 1.88390 |
| H | -0.41670 | -7.89900 | 1.19310 |
| H | 0.17490 | -7.09320 | 2.62240 |
| C | -4.54390 | -3.67370 | 4.67520 |
| H | -4.47710 | -2.78360 | 5.30320 |
| C | -5.43920 | -3.30950 | 3.47600 |
| H | -6.42110 | -2.97610 | 3.81310 |
| H | -5.59740 | -4.16000 | 2.81280 |
| H | -5.01340 | -2.49850 | 2.88530 |
| C | -5.20770 | -4.76110 | 5.53660 |
| H | -6.18760 | -4.43920 | 5.89040 |
| H | -4.60430 | -4.99200 | 6.41500 |
| H | -5.34780 | -5.68770 | 4.97880 |
| O | 0.72310 | -4.80450 | 3.65960 |
| O | -0.28760 | -1.76980 | 3.01680 |
| Si | 1.27810 | -1.16360 | 3.22430 |
| C | 1.83670 | -1.47760 | 4.99700 |
| H | 1.90840 | -2.54460 | 5.20750 |
| H | 1.14220 | -1.04520 | 5.71570 |
| H | 2.81730 | -1.04360 | 5.18670 |
| C | 2.42840 | -2.01140 | 1.99350 |
| H | 2.54390 | -3.07170 | 2.21570 |
| H | 3.42330 | -1.56950 | 2.01290 |
| H | 2.05230 | -1.92670 | 0.97520 |
| C | 1.20310 | 0.70900 | 2.86520 |
| C | 0.71520 | 0.92160 | 1.42210 |
| H | -0.26450 | 0.46730 | 1.26630 |
| H | 1.39950 | 0.47670 | 0.69920 |
| H | 0.62870 | 1.98160 | 1.18210 |
| C | 0.21540 | 1.36360 | 3.84590 |
| H | -0.77860 | 0.92230 | 3.75800 |
| H | 0.11840 | 2.43360 | 3.66050 |
| H | 0.53700 | 1.23800 | 4.88020 |
| C | 2.60120 | 1.32600 | 3.04140 |
| H | 3.32450 | 0.87790 | 2.35960 |
| H | 2.97530 | 1.18350 | 4.05580 |
| H | 2.58890 | 2.39850 | 2.84560 |

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Compound **5.16**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1222.55516756 hartree.
Free Energy: -1222.112793 hartree.

| | | | |
|---|---|---|---|
| C | -1.63830 | -2.68493 | -0.97515 |
| H | -1.69453 | -3.07930 | -1.98986 |
| C | -0.63502 | -1.82985 | -0.70377 |
| H | 0.06098 | -1.55835 | -1.49393 |
| C | -0.44215 | -1.12638 | 0.59118 |
| C | 0.16866 | 0.29219 | 0.54562 |
| H | 0.29887 | 0.57913 | 1.59819 |
| C | -0.69814 | 1.35637 | -0.15640 |
| H | -0.70367 | 1.13468 | -1.23042 |
| H | -0.16376 | 2.30855 | -0.03988 |
| C | -2.15351 | 1.49948 | 0.37460 |
| H | -2.12724 | 1.37833 | 1.46760 |
| C | -2.98243 | 0.37559 | -0.19983 |
| H | -3.07867 | 0.36010 | -1.28586 |
| C | -3.43786 | -0.67828 | 0.48832 |
| H | -3.27426 | -0.71931 | 1.56614 |
| C | -3.87133 | -1.93945 | -0.15596 |
| C | -5.02835 | -2.10495 | -0.80451 |
| H | -5.27833 | -3.04151 | -1.29792 |
| H | -5.76942 | -1.31191 | -0.85045 |
| C | -2.80341 | -3.04284 | -0.07741 |
| H | -3.23731 | -3.99563 | -0.39818 |
| H | -2.46077 | -3.14711 | 0.95525 |
| C | -2.73259 | 2.91853 | 0.10007 |
| H | -2.02296 | 3.62864 | 0.55112 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.84171 | 3.26415 | -1.39385 | C | -0.31570 | 0.09509 | -0.15616 |
| H | -3.18083 | 4.29878 | -1.52126 | H | -0.68548 | 0.40969 | -1.14228 |
| H | -3.56706 | 2.61932 | -1.90421 | C | 0.51933 | 1.22701 | 0.45369 |
| H | -1.88119 | 3.16773 | -1.91220 | H | 0.73854 | 0.95828 | 1.49486 |
| C | -4.08548 | 3.10256 | 0.80195 | H | -0.13486 | 2.10869 | 0.48780 |
| H | -4.46420 | 4.12180 | 0.66205 | C | 1.82548 | 1.56585 | -0.29645 |
| H | -4.00329 | 2.91986 | 1.88019 | H | 1.64019 | 1.46925 | -1.37672 |
| H | -4.83391 | 2.40688 | 0.40461 | C | 2.86202 | 0.54463 | 0.09150 |
| O | -0.72377 | -1.61572 | 1.67830 | H | 3.11050 | 0.48821 | 1.15343 |
| O | 1.42407 | 0.24127 | -0.13279 | C | 3.34417 | -0.39677 | -0.72223 |
| Si | 2.92021 | -0.03656 | 0.60772 | H | 3.03831 | -0.40770 | -1.76942 |
| C | 3.17500 | 1.22026 | 1.99819 | C | 4.01811 | -1.61148 | -0.21343 |
| H | 2.44110 | 1.08292 | 2.80137 | C | 5.24360 | -1.63730 | 0.31103 |
| H | 3.08654 | 2.25160 | 1.63855 | H | 5.66448 | -2.55090 | 0.72446 |
| H | 4.16808 | 1.10850 | 2.45032 | H | 5.86627 | -0.74679 | 0.33142 |
| C | 2.97445 | -1.77839 | 1.33652 | C | 3.10213 | -2.83614 | -0.23307 |
| H | 2.15618 | -1.92530 | 2.05107 | H | 3.68923 | -3.73844 | -0.04101 |
| H | 3.91616 | -1.95882 | 1.86915 | H | 2.62863 | -2.92292 | -1.21336 |
| H | 2.87401 | -2.54880 | 0.56364 | C | 2.26862 | 3.02323 | -0.03770 |
| C | 4.18705 | 0.19639 | -0.80535 | H | 1.43546 | 3.66172 | -0.36390 |
| C | 4.11438 | 1.64098 | -1.34496 | C | 2.53131 | 3.31470 | 1.44077 |
| H | 4.37150 | 2.37901 | -0.57533 | H | 2.77676 | 4.37291 | 1.58178 |
| H | 3.11314 | 1.88108 | -1.71977 | H | 3.37952 | 2.72993 | 1.81516 |
| H | 4.82339 | 1.77520 | -2.17495 | H | 1.66133 | 3.09133 | 2.06737 |
| C | 5.61234 | -0.07757 | -0.27743 | C | 3.49615 | 3.37150 | -0.87780 |
| H | 5.89050 | 0.60645 | 0.53409 | H | 3.75582 | 4.43027 | -0.77134 |
| H | 6.34944 | 0.05706 | -1.08209 | H | 3.32143 | 3.17054 | -1.94092 |
| H | 5.72269 | -1.10309 | 0.09574 | H | 4.36432 | 2.77971 | -0.56459 |
| C | 3.87880 | -0.78281 | -1.95862 | O | 0.66617 | -1.57274 | -1.55348 |
| H | 2.87708 | -0.61665 | -2.37030 | O | -1.38027 | -0.17658 | 0.74064 |
| H | 3.94165 | -1.82996 | -1.63796 | Si | -2.89745 | -0.71668 | 0.24270 |
| H | 4.60237 | -0.64881 | -2.77601 | C | -2.70819 | -1.90820 | -1.19538 |
| | | | | H | -2.06904 | -2.75497 | -0.91965 |
| | | | | H | -2.27189 | -1.44089 | -2.08519 |
| | | | | H | -3.68630 | -2.31533 | -1.47803 |
| | | | | C | -3.59929 | -1.59332 | 1.73857 |
| | | | | H | -3.04796 | -2.52042 | 1.93250 |
| | | | | H | -4.65339 | -1.85809 | 1.59720 |
| | | | | H | -3.52631 | -0.96916 | 2.63571 |
| | | | | C | -3.96810 | 0.77414 | -0.24075 |
| | | | | C | -3.21698 | 1.67625 | -1.22800 |
| | | | | H | -2.92414 | 1.13646 | -2.13737 |
| | | | | H | -2.31161 | 2.10376 | -0.77974 |
| | | | | H | -3.85587 | 2.51596 | -1.53741 |
| | | | | C | -5.26240 | 0.27890 | -0.89916 |
| | | | | H | -5.06307 | -0.25111 | -1.83815 |
| | | | | H | -5.91974 | 1.12806 | -1.13419 |
| | | | | H | -5.82620 | -0.39784 | -0.24442 |

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Compound **5.16**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1222.10250866 hartree.
Free Energy: -1221.658263 hartree.

| | | | |
|---|---|---|---|
| C | -4.31135 | 1.58147 | 1.01813 |
| H | -3.40802 | 1.91097 | 1.54646 |
| H | -4.91819 | 0.99758 | 1.72040 |
| H | -4.88676 | 2.47982 | 0.75295 |

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Compound **5.16**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1222.56872397 hartree.
Free Energy: -1222.129125 hartree.

| | | | |
|---|---|---|---|
| C | -1.98533 | -2.94653 | -0.12538 |
| H | -2.09853 | -3.84570 | 0.48036 |
| C | -0.80115 | -2.31407 | -0.07860 |
| H | -0.02542 | -2.70448 | 0.58048 |
| C | -0.46886 | -1.03729 | -0.77462 |
| C | 0.14677 | 0.10141 | 0.08700 |
| H | 0.06545 | -0.16549 | 1.14977 |
| C | -0.54503 | 1.45174 | -0.17122 |
| H | -0.55414 | 1.60638 | -1.25591 |
| H | 0.09866 | 2.22590 | 0.26272 |
| C | -1.97398 | 1.60759 | 0.41334 |
| H | -1.89155 | 1.54712 | 1.50824 |
| C | -2.82737 | 0.45575 | -0.05034 |
| H | -2.81288 | 0.27219 | -1.12244 |
| C | -3.48605 | -0.40321 | 0.74455 |
| H | -3.54316 | -0.19575 | 1.81424 |
| C | -4.06039 | -1.69078 | 0.29648 |
| C | -5.12987 | -2.24004 | 0.89354 |
| H | -5.51428 | -3.21314 | 0.59689 |
| H | -5.66255 | -1.72698 | 1.69183 |
| C | -3.26330 | -2.45044 | -0.76755 |
| H | -3.04220 | -1.81115 | -1.62552 |
| H | -3.85055 | -3.30162 | -1.12785 |
| C | -2.56689 | 3.01470 | 0.08761 |
| H | -1.77580 | 3.74234 | 0.32253 |
| C | -2.94901 | 3.20155 | -1.38881 |
| H | -3.26174 | 4.23680 | -1.57190 |
| H | -3.78704 | 2.55214 | -1.67091 |
| H | -2.11507 | 2.98741 | -2.06677 |
| C | -3.76650 | 3.32348 | 0.99386 |
| H | -4.15715 | 4.32956 | 0.79732 |
| H | -3.49165 | 3.27492 | 2.05508 |
| H | -4.58463 | 2.61145 | 0.82707 |
| O | -0.63467 | -0.87786 | -1.97567 |
| O | 1.51836 | 0.24984 | -0.28296 |
| Si | 2.86728 | -0.57192 | 0.31371 |
| C | 2.65900 | -0.90372 | 2.16224 |
| H | 1.87200 | -1.64113 | 2.36402 |
| H | 2.41213 | 0.00613 | 2.72258 |
| H | 3.58792 | -1.30678 | 2.58626 |
| C | 3.08555 | -2.20982 | -0.60047 |
| H | 2.22342 | -2.87142 | -0.45035 |
| H | 3.97315 | -2.74809 | -0.24436 |
| H | 3.19829 | -2.05924 | -1.68079 |
| C | 4.33758 | 0.60540 | -0.02662 |
| C | 4.21536 | 1.87101 | 0.84774 |
| H | 4.24653 | 1.63411 | 1.91881 |
| H | 3.28368 | 2.41619 | 0.65332 |
| H | 5.04781 | 2.56067 | 0.64225 |
| C | 5.66515 | -0.10754 | 0.30939 |
| H | 5.70953 | -0.42959 | 1.35784 |
| H | 6.51551 | 0.57062 | 0.14388 |
| H | 5.82940 | -0.99170 | -0.31865 |
| C | 4.34959 | 1.01786 | -1.51348 |
| H | 3.42716 | 1.53601 | -1.79908 |
| H | 4.46436 | 0.15278 | -2.17904 |
| H | 5.19033 | 1.69825 | -1.71671 |

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Compound **5.16**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1222.57050343 hartree.
Free Energy: -1222.128149 hartree.

| | | | |
|---|---|---|---|
| C | -1.76820 | -2.62672 | -1.07903 |
| H | -1.87515 | -2.97249 | -2.10708 |
| C | -0.72706 | -1.81629 | -0.80940 |
| H | -0.05869 | -1.53038 | -1.61856 |
| C | -0.45812 | -1.18048 | 0.50698 |
| C | 0.17192 | 0.23078 | 0.51048 |
| H | 0.31672 | 0.47774 | 1.56998 |
| C | -0.66926 | 1.34083 | -0.14786 |
| H | -0.70944 | 1.15226 | -1.22746 |
| H | -0.10094 | 2.27024 | -0.01246 |
| C | -2.10498 | 1.52195 | 0.42255 |
| H | -2.05531 | 1.38401 | 1.51236 |
| C | -2.98185 | 0.43625 | -0.15248 |

| | | | |
|---|---|---|---|
| H | -3.11319 | 0.45680 | -1.23474 |
| C | -3.44896 | -0.62365 | 0.51989 |
| H | -3.25866 | -0.70173 | 1.59164 |
| C | -3.94591 | -1.84777 | -0.15156 |
| C | -5.12994 | -1.95278 | -0.76484 |
| H | -5.42564 | -2.86188 | -1.28502 |
| H | -5.84854 | -1.13654 | -0.75652 |
| C | -2.91291 | -2.98645 | -0.15692 |
| H | -3.38780 | -3.90966 | -0.50348 |
| H | -2.54458 | -3.14598 | 0.85975 |
| C | -2.64422 | 2.96327 | 0.18178 |
| H | -1.89709 | 3.64287 | 0.61804 |
| C | -2.78929 | 3.33253 | -1.30283 |
| H | -3.09703 | 4.38035 | -1.40531 |
| H | -3.55106 | 2.72040 | -1.80109 |
| H | -1.84877 | 3.21366 | -1.85307 |
| C | -3.96657 | 3.18563 | 0.92791 |
| H | -4.30897 | 4.22203 | 0.81851 |
| H | -3.86088 | 2.98075 | 2.00071 |
| H | -4.75781 | 2.53057 | 0.54227 |
| O | -0.67488 | -1.73520 | 1.57992 |
| O | 1.42704 | 0.17974 | -0.17091 |
| Si | 2.90648 | -0.31150 | 0.49511 |
| C | 3.05278 | 0.33150 | 2.26468 |
| H | 2.36165 | -0.18565 | 2.94165 |
| H | 2.84598 | 1.40610 | 2.33439 |
| H | 4.06553 | 0.16518 | 2.65434 |
| C | 3.01462 | -2.19662 | 0.50509 |
| H | 2.20499 | -2.63317 | 1.10268 |
| H | 3.96068 | -2.53787 | 0.94446 |
| H | 2.94354 | -2.61968 | -0.50428 |
| C | 4.22428 | 0.45953 | -0.65833 |
| C | 3.93744 | 0.07150 | -2.12413 |
| H | 2.95674 | 0.43089 | -2.45649 |
| H | 3.96212 | -1.01545 | -2.27424 |
| H | 4.69499 | 0.50789 | -2.79253 |
| C | 4.20151 | 1.99690 | -0.52910 |
| H | 3.22101 | 2.41377 | -0.78930 |
| H | 4.94137 | 2.45098 | -1.20526 |
| H | 4.44644 | 2.32667 | 0.48840 |
| C | 5.62507 | -0.05894 | -0.26801 |
| H | 5.70658 | -1.14742 | -0.37722 |
| H | 5.88842 | 0.19312 | 0.76735 |
| H | 6.39267 | 0.39067 | -0.91533 |

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Compound **5.16**
This structure was assigned as correct.

B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1222.55282476 hartree.
Free Energy: -1222.111088 hartree.

| | | | |
|---|---|---|---|
| C | -2.00546 | -3.07257 | -0.14613 |
| H | -2.08741 | -3.97089 | 0.46569 |
| C | -0.81556 | -2.45528 | -0.19165 |
| H | 0.01334 | -2.85183 | 0.39426 |
| C | -0.55870 | -1.16498 | -0.89604 |
| C | 0.06061 | -0.02176 | -0.04610 |
| H | -0.10214 | -0.24608 | 1.01908 |
| C | -0.54081 | 1.34926 | -0.39079 |
| H | -0.52384 | 1.44654 | -1.48297 |
| H | 0.13627 | 2.10696 | 0.01564 |
| C | -1.98187 | 1.59768 | 0.14390 |
| H | -1.93083 | 1.69526 | 1.24010 |
| C | -2.83194 | 0.39743 | -0.18597 |
| H | -2.88279 | 0.15748 | -1.24632 |
| C | -3.41634 | -0.42473 | 0.69988 |
| H | -3.40660 | -0.15111 | 1.75623 |
| C | -4.01832 | -1.73585 | 0.37243 |
| C | -5.03737 | -2.24142 | 1.08379 |
| H | -5.45143 | -3.22412 | 0.87367 |
| H | -5.49948 | -1.68087 | 1.89283 |
| C | -3.31580 | -2.55864 | -0.70908 |
| H | -3.13408 | -1.96389 | -1.60731 |
| H | -3.94981 | -3.40407 | -0.99705 |
| C | -2.58472 | 2.91754 | -0.42078 |
| H | -2.67898 | 2.78903 | -1.51022 |
| C | -3.98831 | 3.17385 | 0.14934 |
| H | -4.42861 | 4.07482 | -0.29341 |
| H | -3.94659 | 3.32608 | 1.23630 |
| H | -4.66435 | 2.33494 | -0.04286 |
| C | -1.68356 | 4.13641 | -0.16590 |
| H | -2.17176 | 5.05220 | -0.51895 |
| H | -0.72013 | 4.06017 | -0.67920 |
| H | -1.48607 | 4.26191 | 0.90724 |
| O | -0.79912 | -0.99622 | -2.07946 |
| O | 1.45387 | -0.03306 | -0.36038 |
| Si | 2.74075 | -0.08380 | 0.72499 |
| C | 2.66418 | 1.40323 | 1.89305 |
| H | 1.73766 | 1.39676 | 2.48071 |
| H | 2.70267 | 2.35272 | 1.34746 |
| H | 3.49768 | 1.39315 | 2.60602 |
| C | 2.64781 | -1.66341 | 1.76388 |

| | | | |
|---|---|---|---|
| H | 1.71565 | -1.70663 | 2.34103 |
| H | 3.47294 | -1.71227 | 2.48487 |
| H | 2.69609 | -2.56446 | 1.14182 |
| C | 4.28765 | -0.05027 | -0.39436 |
| C | 5.56760 | -0.11539 | 0.46704 |
| H | 5.62102 | -1.03743 | 1.05933 |
| H | 5.64375 | 0.73286 | 1.15900 |
| H | 6.45977 | -0.09055 | -0.17495 |
| C | 4.25781 | -1.25776 | -1.35660 |
| H | 4.28305 | -2.21320 | -0.81784 |
| H | 5.13362 | -1.23649 | -2.02138 |
| H | 3.36076 | -1.24907 | -1.98490 |
| C | 4.30051 | 1.25035 | -1.22664 |
| H | 4.35910 | 2.14307 | -0.59164 |
| H | 3.40371 | 1.33753 | -1.84953 |
| H | 5.17486 | 1.26673 | -1.89339 |

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Compound **5.16**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1222.10169296 hartree.
Free Energy: -1221.656511 hartree.

| | | | |
|---|---|---|---|
| C | -1.94848 | -3.07145 | -0.28824 |
| H | -1.96593 | -4.00194 | 0.27790 |
| C | -0.77123 | -2.46014 | -0.45270 |
| H | 0.12940 | -2.88279 | -0.00776 |
| C | -0.61494 | -1.12996 | -1.11028 |
| C | 0.05073 | -0.03295 | -0.25421 |
| H | -0.12134 | -0.28102 | 0.80628 |
| C | -0.50652 | 1.35792 | -0.54528 |
| H | -0.57800 | 1.48082 | -1.63324 |
| H | 0.21983 | 2.08859 | -0.17485 |
| C | -1.88242 | 1.61065 | 0.11363 |
| H | -1.72742 | 1.70786 | 1.20008 |
| C | -2.75626 | 0.41229 | -0.13292 |
| H | -2.97049 | 0.20883 | -1.18294 |
| C | -3.17956 | -0.44187 | 0.80565 |
| H | -2.99633 | -0.20514 | 1.85507 |
| C | -3.83788 | -1.73959 | 0.52680 |
| C | -4.74145 | -2.26005 | 1.36287 |
| H | -5.19209 | -3.23264 | 1.18281 |
| H | -5.06326 | -1.72193 | 2.25147 |
| C | -3.30608 | -2.52200 | -0.66589 |
| H | -3.23108 | -1.88712 | -1.55242 |
| H | -3.98597 | -3.34636 | -0.89894 |
| C | -2.53541 | 2.91295 | -0.39555 |
| H | -2.72752 | 2.78281 | -1.47120 |
| C | -3.86997 | 3.15792 | 0.30848 |
| H | -4.33962 | 4.07796 | -0.05520 |
| H | -3.71896 | 3.26395 | 1.39050 |
| H | -4.57156 | 2.33336 | 0.14816 |
| C | -1.61620 | 4.12078 | -0.21379 |
| H | -2.12729 | 5.04029 | -0.51877 |
| H | -0.70040 | 4.04037 | -0.80667 |
| H | -1.32925 | 4.23324 | 0.83988 |
| O | -0.95383 | -0.91405 | -2.25563 |
| O | 1.43357 | -0.11103 | -0.57580 |
| Si | 2.58761 | -0.12616 | 0.65169 |
| C | 2.29869 | 1.33911 | 1.78975 |
| H | 1.32508 | 1.26622 | 2.28991 |
| H | 2.32698 | 2.28992 | 1.24695 |
| H | 3.06294 | 1.37742 | 2.57526 |
| C | 2.42682 | -1.71632 | 1.63604 |
| H | 1.40878 | -1.84352 | 2.02349 |
| H | 3.10098 | -1.70836 | 2.50060 |
| H | 2.66868 | -2.59767 | 1.03145 |
| C | 4.25225 | -0.01852 | -0.23213 |
| C | 5.37992 | -0.28726 | 0.77375 |
| H | 5.32161 | -1.30087 | 1.18834 |
| H | 5.36141 | 0.42169 | 1.61125 |
| H | 6.35808 | -0.18730 | 0.28285 |
| C | 4.31627 | -1.06223 | -1.35467 |
| H | 4.19964 | -2.08242 | -0.96890 |
| H | 5.29020 | -1.01229 | -1.86204 |
| H | 3.53727 | -0.89605 | -2.10635 |
| C | 4.42874 | 1.38273 | -0.83193 |
| H | 4.46424 | 2.15517 | -0.05441 |
| H | 3.61407 | 1.63427 | -1.52163 |
| H | 5.37075 | 1.43937 | -1.39548 |

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Compound **5.17**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +50.997051 kJ.

| | | | |
|---|---|---|---|
| C | -3.45000 | 4.44760 | -8.45570 |
| C | -2.05780 | 4.47950 | -9.09930 |
| C | -3.77290 | 7.29810 | -6.67960 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.40440 | 5.89650 | -6.54340 | H | -3.89230 | 7.15290 | -6.44560 |
| C | -3.46390 | 4.72470 | -6.92650 | H | -1.76950 | 4.97090 | -6.07480 |
| H | -4.08110 | 5.16740 | -8.97440 | H | -3.13630 | 5.11650 | -5.03600 |
| H | -3.88670 | 3.47140 | -8.66540 | H | -3.35570 | 3.36630 | -6.77330 |
| H | -2.98220 | 7.40280 | -5.94030 | C | -2.31850 | 7.75970 | -8.65430 |
| H | -4.51330 | 8.05910 | -6.43150 | C | -1.61190 | 5.19370 | -10.31920 |
| H | -4.70950 | 5.78560 | -5.50170 | C | -0.66140 | 6.39750 | -10.09030 |
| H | -5.32850 | 5.83930 | -7.12030 | C | -1.35430 | 7.76110 | -9.83040 |
| H | -2.46040 | 5.00060 | -6.59480 | H | -0.60500 | 8.53570 | -9.66170 |
| C | -1.98500 | 7.67010 | -8.48470 | H | -1.89160 | 8.05620 | -10.73290 |
| C | -1.92600 | 5.16020 | -10.46600 | H | -2.51340 | 5.51030 | -10.84340 |
| C | -0.99870 | 6.39890 | -10.47530 | H | -1.11640 | 4.47360 | -10.97050 |
| C | -1.63950 | 7.70950 | -9.96360 | H | 0.04270 | 6.16820 | -9.28900 |
| H | -0.95590 | 8.54260 | -10.13260 | H | -0.03920 | 6.50630 | -10.97890 |
| H | -2.53050 | 7.93370 | -10.55170 | C | -3.69440 | 8.32720 | -8.96320 |
| H | -2.91160 | 5.41950 | -10.85130 | H | -4.22060 | 7.68760 | -9.67170 |
| H | -1.51920 | 4.41100 | -11.14520 | H | -4.31920 | 8.44630 | -8.08080 |
| H | -0.08450 | 6.18420 | -9.91930 | H | -3.59260 | 9.31480 | -9.41370 |
| H | -0.67320 | 6.56350 | -11.50260 | C | -1.96860 | 7.19110 | -7.48390 |
| C | -0.78520 | 7.61050 | -7.55160 | H | -0.95740 | 6.82450 | -7.37860 |
| H | 0.00320 | 8.27290 | -7.90920 | O | -1.16370 | 3.72590 | -8.46330 |
| H | -1.01780 | 7.92300 | -6.53610 | C | -5.14680 | 4.49640 | -6.67720 |
| H | -0.38220 | 6.59810 | -7.51320 | H | -5.72680 | 3.77550 | -7.25420 |
| C | -3.26900 | 7.57140 | -8.08500 | H | -5.33700 | 4.29380 | -5.62270 |
| H | -4.04390 | 7.58700 | -8.83790 | H | -5.53900 | 5.48870 | -6.90090 |
| O | -1.08330 | 3.96340 | -8.55520 | | | | |
| C | -3.82450 | 3.44440 | -6.15540 | | | | |
| H | -3.13450 | 2.63540 | -6.39950 | | | | |
| H | -3.76800 | 3.60210 | -5.07780 | | | | |
| H | -4.83400 | 3.10600 | -6.39070 | | | | |

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Compound **5.17**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +58.676735 kJ.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -3.42940 | 4.57700 | -8.53220 | C | -3.30671 | 4.32372 | -8.31515 |
| C | -1.98910 | 4.42950 | -9.04270 | C | -1.97481 | 4.84028 | -8.83614 |
| C | -2.86430 | 6.82290 | -6.31820 | C | -3.43976 | 7.10731 | -6.65308 |
| C | -2.81000 | 5.30030 | -6.06060 | C | -4.25461 | 5.81931 | -6.46124 |
| C | -3.64770 | 4.39220 | -7.00590 | C | -3.54899 | 4.49741 | -6.80699 |
| H | -3.81010 | 5.54790 | -8.84040 | H | -4.13145 | 4.75420 | -8.89390 |
| H | -4.02870 | 3.84090 | -9.06730 | H | -3.29248 | 3.25004 | -8.56211 |
| H | -2.48120 | 7.34740 | -5.44240 | H | -2.51620 | 7.03045 | -6.06912 |
| | | | | H | -4.01968 | 7.93482 | -6.21981 |
| | | | | H | -4.56029 | 5.77246 | -5.40845 |

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Compound **5.17**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -544.297266402 hartree.
Free Energy: -544.035506 hartree.

| | | | |
|---|---|---|---|
| H | -5.18332 | 5.88378 | -7.04804 |
| H | -2.56993 | 4.47996 | -6.31000 |
| C | -1.92933 | 7.74240 | -8.59476 |
| C | -1.91133 | 5.25492 | -10.30087 |
| C | -1.02975 | 6.47802 | -10.56097 |
| C | -1.70648 | 7.77787 | -10.08611 |
| H | -1.07865 | 8.63374 | -10.36280 |
| H | -2.66464 | 7.88532 | -10.60971 |
| H | -2.92238 | 5.42572 | -10.68651 |
| H | -1.50725 | 4.38578 | -10.83846 |
| H | -0.06943 | 6.34115 | -10.05017 |
| H | -0.81807 | 6.55128 | -11.63310 |
| C | -0.69349 | 7.91836 | -7.74940 |
| H | -0.00383 | 8.62827 | -8.21886 |
| H | -0.92105 | 8.28530 | -6.74578 |
| H | -0.16486 | 6.96178 | -7.64763 |
| C | -3.12582 | 7.40751 | -8.09260 |
| H | -3.96057 | 7.29434 | -8.78933 |
| O | -0.96746 | 4.79841 | -8.15396 |
| C | -4.38604 | 3.32873 | -6.28160 |
| H | -3.88779 | 2.37063 | -6.46449 |
| H | -4.56460 | 3.41904 | -5.20478 |
| H | -5.36295 | 3.29770 | -6.78089 |

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Compound **5.17**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -544.552848256 hartree.
Free Energy: -544.293818 hartree.

| | | | |
|---|---|---|---|
| C | -3.31800 | 4.27377 | -8.33163 |
| C | -1.99129 | 4.76734 | -8.90435 |
| C | -3.55409 | 7.17167 | -6.68331 |
| C | -4.31485 | 5.83521 | -6.52287 |
| C | -3.54156 | 4.52783 | -6.81911 |
| H | -4.15699 | 4.65901 | -8.92062 |
| H | -3.29812 | 3.18672 | -8.51187 |
| H | -2.70210 | 7.18133 | -5.99497 |
| H | -4.23322 | 7.96967 | -6.34393 |
| H | -4.66693 | 5.79080 | -5.48329 |
| H | -5.22132 | 5.85696 | -7.14673 |
| H | -2.55138 | 4.58624 | -6.34752 |
| C | -1.87836 | 7.72333 | -8.54997 |
| C | -1.97260 | 5.25498 | -10.35388 |
| C | -1.04782 | 6.45749 | -10.59890 |
| C | -1.62303 | 7.78309 | -10.04293 |
| H | -0.91983 | 8.59331 | -10.28054 |
| H | -2.55919 | 8.00380 | -10.57202 |
| H | -2.99057 | 5.47477 | -10.69445 |
| H | -1.61977 | 4.40118 | -10.95205 |
| H | -0.06976 | 6.24807 | -10.15135 |
| H | -0.88506 | 6.57111 | -11.67790 |
| C | -0.65543 | 7.87070 | -7.67965 |
| H | -0.13938 | 8.81443 | -7.90421 |
| H | -0.88368 | 7.86280 | -6.61104 |
| H | 0.06009 | 7.06117 | -7.87303 |
| C | -3.11614 | 7.45722 | -8.09377 |
| H | -3.91773 | 7.39912 | -8.83401 |
| O | -0.95112 | 4.65415 | -8.26937 |
| C | -4.29237 | 3.34063 | -6.19274 |
| H | -3.74640 | 2.40142 | -6.34461 |
| H | -4.42617 | 3.48026 | -5.11300 |
| H | -5.28981 | 3.22044 | -6.63717 |

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Compound **5.17**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -544.538780175 hartree.
Free Energy: -544.278509 hartree.

| | | | |
|---|---|---|---|
| C | -3.32109 | 4.28229 | -8.33766 |
| C | -1.99076 | 4.77824 | -8.90698 |
| C | -3.56134 | 7.17634 | -6.68505 |
| C | -4.31475 | 5.83597 | -6.52231 |
| C | -3.53488 | 4.53376 | -6.82379 |
| H | -4.16078 | 4.67353 | -8.92310 |
| H | -3.30846 | 3.19587 | -8.52100 |
| H | -2.70421 | 7.18419 | -6.00365 |
| H | -4.23883 | 7.97245 | -6.33849 |
| H | -4.66245 | 5.78845 | -5.48141 |
| H | -5.22616 | 5.85316 | -7.13992 |
| H | -2.53894 | 4.60042 | -6.36678 |
| C | -1.88915 | 7.72077 | -8.55050 |
| C | -1.96517 | 5.25896 | -10.36187 |
| C | -1.04360 | 6.46595 | -10.59748 |
| C | -1.63326 | 7.78561 | -10.04247 |
| H | -0.93967 | 8.60445 | -10.27860 |

| | | | |
|---|---|---|---|
| H | -2.57109 | 7.99923 | -10.57217 |
| H | -2.98154 | 5.47429 | -10.71220 |
| H | -1.60247 | 4.40716 | -10.95646 |
| H | -0.07208 | 6.25673 | -10.13661 |
| H | -0.86789 | 6.58241 | -11.67421 |
| C | -0.66475 | 7.83652 | -7.67553 |
| H | -0.05113 | 8.69102 | -7.98888 |
| H | -0.90806 | 7.97167 | -6.61919 |
| H | -0.04360 | 6.93561 | -7.76045 |
| C | -3.12913 | 7.46694 | -8.09594 |
| H | -3.93457 | 7.42452 | -8.83343 |
| O | -0.95768 | 4.67979 | -8.26519 |
| C | -4.27083 | 3.34126 | -6.18888 |
| H | -3.72116 | 2.40620 | -6.34852 |
| H | -4.39131 | 3.47929 | -5.10800 |
| H | -5.27325 | 3.21697 | -6.62011 |

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Compound **5.17**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -544.292276507 hartree.
Free Energy: -544.029851 hartree.

| | | | |
|---|---|---|---|
| C | -3.47799 | 4.64037 | -8.46628 |
| C | -2.04785 | 4.63879 | -8.96444 |
| C | -2.88088 | 6.79914 | -6.36652 |
| C | -2.82136 | 5.29103 | -6.05075 |
| C | -3.64760 | 4.36569 | -6.96720 |
| H | -3.95210 | 5.58855 | -8.74450 |
| H | -4.00929 | 3.86569 | -9.04137 |
| H | -2.56200 | 7.34440 | -5.46819 |
| H | -3.91263 | 7.10777 | -6.56476 |
| H | -1.77293 | 4.97484 | -6.07774 |
| H | -3.17118 | 5.13083 | -5.02313 |
| H | -3.29446 | 3.34395 | -6.77787 |
| C | -2.26983 | 7.71058 | -8.68603 |
| C | -1.73880 | 5.31063 | -10.29825 |
| C | -0.65530 | 6.39775 | -10.15984 |
| C | -1.22646 | 7.77786 | -9.79062 |
| H | -0.40116 | 8.44437 | -9.51020 |
| H | -1.68836 | 8.21707 | -10.68304 |
| H | -2.64913 | 5.72091 | -10.75005 |
| H | -1.37131 | 4.51491 | -10.95701 |
| H | 0.06058 | 6.06211 | -9.40104 |
| H | -0.09699 | 6.48603 | -11.09778 |
| C | -3.63659 | 8.20680 | -9.07290 |
| H | -4.01123 | 7.65792 | -9.94800 |
| H | -4.37577 | 8.12171 | -8.27339 |
| H | -3.58412 | 9.26149 | -9.37205 |
| C | -1.96700 | 7.15402 | -7.50763 |
| H | -0.93290 | 6.83181 | -7.35882 |
| O | -1.15980 | 4.07578 | -8.35136 |
| C | -5.13494 | 4.42626 | -6.61508 |
| H | -5.71970 | 3.74110 | -7.23911 |
| H | -5.30220 | 4.15353 | -5.56764 |
| H | -5.53813 | 5.43513 | -6.76762 |

---

Compound **5.17**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -544.531660836 hartree.
Free Energy: -544.271141 hartree.

| | | | |
|---|---|---|---|
| C | -3.43749 | 4.55394 | -8.48431 |
| C | -1.98854 | 4.55297 | -8.95591 |
| C | -2.87006 | 6.81227 | -6.35170 |
| C | -2.84280 | 5.29306 | -6.04378 |
| C | -3.65637 | 4.35090 | -6.96912 |
| H | -3.92866 | 5.46826 | -8.83376 |
| H | -3.93828 | 3.73231 | -9.02390 |
| H | -2.49629 | 7.33522 | -5.45863 |
| H | -3.89925 | 7.15928 | -6.49829 |
| H | -1.79859 | 4.96243 | -6.04804 |
| H | -3.21128 | 5.13881 | -5.02056 |
| H | -3.31147 | 3.33600 | -6.73167 |
| C | -2.30691 | 7.74834 | -8.68555 |
| C | -1.65590 | 5.22086 | -10.29672 |
| C | -0.65869 | 6.39914 | -10.15785 |
| C | -1.31818 | 7.75999 | -9.84821 |
| H | -0.52712 | 8.50509 | -9.67731 |
| H | -1.84733 | 8.09727 | -10.74983 |
| H | -2.56560 | 5.54418 | -10.81732 |
| H | -1.18610 | 4.44098 | -10.90901 |
| H | 0.07417 | 6.12984 | -9.38877 |
| H | -0.09346 | 6.50129 | -11.09266 |
| C | -3.63654 | 8.40221 | -8.97312 |
| H | -4.15476 | 7.90337 | -9.80535 |

| | | | |
|---|---|---|---|
| H | -4.30919 | 8.41259 | -8.11213 |
| H | -3.48634 | 9.44426 | -9.28845 |
| C | -1.99216 | 7.14301 | -7.53047 |
| H | -0.98258 | 6.74080 | -7.43778 |
| O | -1.10641 | 3.99712 | -8.32267 |
| C | -5.16151 | 4.41585 | -6.66199 |
| H | -5.72642 | 3.70423 | -7.27672 |
| H | -5.35829 | 4.17796 | -5.61009 |
| H | -5.57099 | 5.41496 | -6.85853 |

---

Compound **5.17**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -544.546351411 hartree.
Free Energy: -544.286407 hartree.

| | | | |
|---|---|---|---|
| C | -3.42506 | 4.27169 | -8.23538 |
| C | -2.65719 | 5.02368 | -9.32328 |
| C | -3.88645 | 7.19567 | -7.04650 |
| C | -4.02534 | 5.87244 | -6.25243 |
| C | -3.22859 | 4.63776 | -6.74242 |
| H | -4.48655 | 4.31269 | -8.50693 |
| H | -3.11090 | 3.22242 | -8.35941 |
| H | -4.26603 | 8.00754 | -6.40702 |
| H | -4.54142 | 7.16781 | -7.92429 |
| H | -3.71342 | 6.05415 | -5.21452 |
| H | -5.09162 | 5.60958 | -6.20587 |
| H | -2.16190 | 4.83273 | -6.57708 |
| C | -2.03758 | 7.88371 | -8.67509 |
| C | -1.12896 | 5.09045 | -9.24867 |
| C | -0.50556 | 6.32015 | -9.93059 |
| C | -0.60677 | 7.62232 | -9.08907 |
| H | 0.02553 | 7.51192 | -8.19859 |
| H | -0.19641 | 8.45264 | -9.67981 |
| H | -0.78119 | 4.18185 | -9.76510 |
| H | -0.78575 | 4.99937 | -8.21311 |
| H | 0.55377 | 6.11943 | -10.13302 |
| H | -0.99192 | 6.46116 | -10.90216 |
| C | -2.93391 | 8.49292 | -9.72263 |
| H | -3.00115 | 7.85052 | -10.60915 |
| H | -3.94955 | 8.67121 | -9.35901 |
| H | -2.52434 | 9.45841 | -10.05119 |
| C | -2.46418 | 7.43265 | -7.48175 |
| H | -1.70301 | 7.07320 | -6.78711 |
| O | -3.24629 | 5.41023 | -10.32491 |
| C | -3.60541 | 3.42853 | -5.86861 |
| H | -2.97236 | 2.56143 | -6.09340 |
| H | -3.49071 | 3.66025 | -4.80259 |
| H | -4.64959 | 3.13162 | -6.03310 |

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Compound **5.17**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -52.023094 kJ.

| | | | |
|---|---|---|---|
| C | -3.94260 | -0.60290 | -6.69070 |
| C | -3.22710 | 0.56710 | -7.45000 |
| C | -4.03670 | 1.19420 | -8.63900 |
| C | -1.85750 | 0.17060 | -8.05360 |
| H | -3.05140 | 1.32790 | -6.69010 |
| H | -1.58110 | -0.83110 | -7.73600 |
| C | -0.70430 | 1.12610 | -7.64420 |
| C | -5.53030 | 0.67220 | -8.63400 |
| C | -3.23150 | 0.67550 | -9.85520 |
| C | -3.95370 | 2.76430 | -8.57490 |
| H | -6.00170 | 1.04250 | -7.72290 |
| C | -5.57370 | -0.83770 | -8.51000 |
| C | -6.43420 | 1.11630 | -9.78090 |
| C | -4.79840 | -1.47000 | -7.61630 |
| O | -4.65410 | 3.23120 | -7.41910 |
| O | -3.69430 | 0.73370 | -10.99450 |
| N | -2.04320 | 0.14190 | -9.50610 |
| H | -0.95200 | 2.16360 | -7.86860 |
| C | -7.54320 | 1.85710 | -9.61110 |
| C | -8.38970 | 2.43080 | -10.73180 |
| H | -7.84450 | 2.13290 | -8.61060 |
| C | -8.43100 | 3.97660 | -10.71230 |
| H | -9.39950 | 2.04210 | -10.59670 |
| H | -8.04650 | 2.06650 | -11.70150 |
| H | -9.41660 | 4.29940 | -11.02860 |
| C | -7.33440 | 4.64020 | -11.55930 |
| H | -8.36580 | 4.34600 | -9.68870 |
| C | -6.02840 | 4.73160 | -11.21840 |
| O | -7.70320 | 5.16730 | -12.77430 |
| C | -5.56240 | 4.19520 | -9.95400 |
| C | -4.42180 | 3.49300 | -9.83340 |
| H | -6.18900 | 4.31600 | -9.08350 |
| H | -3.81070 | 3.35010 | -10.71310 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Si | -9.16860 | 5.21030 | -13.62970 | H | -6.84510 | 4.87660 | -15.46460 |
| C | -9.88260 | 3.46940 | -13.81170 | C | -8.14090 | 7.31280 | -15.19800 |
| C | -10.38670 | 6.36340 | -12.75530 | H | -7.86410 | 7.74110 | -16.16160 |
| C | -8.76370 | 5.91540 | -15.36020 | H | -7.23960 | 7.27410 | -14.58410 |
| H | -11.29620 | 6.49420 | -13.33920 | H | -8.83220 | 8.00600 | -14.71800 |
| H | -9.94930 | 7.34980 | -12.60760 | C | -10.04960 | 6.01280 | -16.19990 |
| H | -10.68150 | 5.99180 | -11.77650 | H | -9.84420 | 6.41370 | -17.19290 |
| H | -10.71890 | 3.45360 | -14.50840 | H | -10.78520 | 6.66660 | -15.73060 |
| H | -10.24470 | 3.07410 | -12.86530 | H | -10.51580 | 5.03630 | -16.33330 |
| H | -9.12980 | 2.77800 | -14.18800 | C | -0.33010 | 0.99600 | -6.17940 |
| C | -4.06700 | 4.06970 | -6.55080 | C | 0.35600 | 0.72630 | -3.45530 |
| O | -2.91690 | 4.49770 | -6.62270 | C | -0.65490 | 2.01740 | -5.26200 |
| C | -4.98650 | 4.45320 | -5.40350 | C | 0.34970 | -0.15570 | -5.72950 |
| H | -5.26770 | 3.56780 | -4.83430 | C | 0.68960 | -0.29140 | -4.36970 |
| H | -5.89020 | 4.92590 | -5.78720 | C | -0.31440 | 1.88120 | -3.90240 |
| H | -4.48510 | 5.15260 | -4.73480 | H | -1.16440 | 2.91030 | -5.59340 |
| H | -6.12780 | 0.85990 | -10.78510 | H | 0.60780 | -0.94110 | -6.42650 |
| C | -3.07100 | -1.35320 | -5.66330 | H | 1.20770 | -1.17610 | -4.02910 |
| H | -4.68860 | -0.10820 | -6.06540 | H | -0.56530 | 2.66570 | -3.20330 |
| C | -4.87180 | -2.98030 | -7.43330 | H | 0.61850 | 0.62320 | -2.41240 |
| H | -6.24430 | -1.38540 | -9.15810 | C | -1.14300 | -0.49000 | -10.31100 |
| H | -2.38920 | -2.06600 | -6.12220 | O | -0.24950 | -1.19720 | -9.84050 |
| H | -3.68490 | -1.90140 | -4.94900 | C | -1.17810 | -0.33580 | -11.80910 |
| H | -2.47370 | -0.65340 | -5.07840 | C | -1.14940 | -0.08970 | -14.62550 |
| Si | -3.79070 | -3.97660 | -8.63980 | C | -1.08950 | 0.93970 | -12.41440 |
| H | -5.90980 | -3.26790 | -7.60190 | C | -1.21720 | -1.48640 | -12.62670 |
| H | -4.68390 | -3.26930 | -6.40160 | C | -1.21110 | -1.36430 | -14.03020 |
| C | -4.39010 | -5.76520 | -8.62850 | C | -1.08490 | 1.06200 | -13.81800 |
| C | -3.96610 | -3.30070 | -10.39460 | H | -1.03380 | 1.82850 | -11.80310 |
| C | -1.97250 | -3.97410 | -8.14100 | H | -1.25390 | -2.46680 | -12.17250 |
| H | -5.43460 | -5.83970 | -8.92970 | H | -1.25060 | -2.24860 | -14.64970 |
| H | -4.30490 | -6.20870 | -7.63680 | H | -1.03100 | 2.03930 | -14.27550 |
| H | -3.81020 | -6.38490 | -9.31190 | H | -1.14580 | 0.00420 | -15.70180 |
| H | -4.99700 | -3.35650 | -10.74260 | | | | |
| H | -3.35490 | -3.86000 | -11.10210 | ---------- | | | |
| H | -3.66410 | -2.25750 | -10.46080 | | | | |
| H | -1.52030 | -2.99150 | -8.24760 | Compound **5.18** | | | |
| H | -1.39010 | -4.65330 | -8.76280 | This structure was assigned as ambiguous. | | | |
| H | -1.83760 | -4.28790 | -7.10660 | | | | |
| H | -2.89840 | 3.02360 | -8.49230 | Molecular Mechanics (OPLS-2005), gas | | | |
| C | -5.04650 | 5.41650 | -12.15470 | phase. | | | |
| H | -5.44980 | 6.36610 | -12.50790 | Energy: -39.918869 kJ. | | | |
| H | -4.85370 | 4.78360 | -13.02100 | | | | |
| H | -4.09830 | 5.62470 | -11.65940 | C | -4.63950 | -0.74170 | -6.38300 |
| H | 0.19890 | 0.90870 | -8.21600 | C | -3.67860 | 0.17320 | -7.19850 |
| C | -7.75730 | 4.98150 | -16.05430 | C | -4.30030 | 0.84790 | -8.47180 |
| H | -7.47250 | 5.35930 | -17.03650 | C | -2.40960 | -0.57550 | -7.66520 |
| H | -8.17020 | 3.98200 | -16.19450 | H | -3.36550 | 0.95630 | -6.51120 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.59320 | -1.64360 | -7.56640 | H | -6.46750 | -1.81370 | -9.11820 |
| C | -1.14920 | -0.22510 | -6.81580 | H | -3.25150 | -2.13810 | -5.39500 |
| C | -5.75100 | 0.27820 | -8.77210 | H | -4.72170 | -1.82250 | -4.47950 |
| C | -3.26700 | 0.46140 | -9.56120 | H | -3.46720 | -0.61420 | -4.54940 |
| C | -4.32830 | 2.41100 | -8.28290 | Si | -4.39400 | -4.40370 | -7.69430 |
| H | -6.44920 | 0.77260 | -8.09610 | H | -6.60840 | -3.41670 | -7.26710 |
| C | -5.89290 | -1.19500 | -8.44240 | H | -5.66790 | -3.27710 | -5.84140 |
| C | -6.28280 | 0.53340 | -10.17320 | C | -5.22010 | -6.09960 | -7.69120 |
| C | -5.37420 | -1.70460 | -7.31500 | C | -4.01840 | -3.92620 | -9.48190 |
| O | -5.12560 | 2.71600 | -7.13300 | C | -2.78530 | -4.54890 | -6.71470 |
| O | -3.41830 | 0.81600 | -10.73110 | H | -4.57540 | -6.85810 | -8.13480 |
| N | -2.26430 | -0.31050 | -9.09740 | H | -6.15050 | -6.09330 | -8.25820 |
| H | -1.40360 | -0.15150 | -5.75820 | H | -5.45760 | -6.42720 | -6.67940 |
| C | -7.25610 | 1.40900 | -10.46560 | H | -3.57230 | -2.93610 | -9.54560 |
| C | -7.54410 | 1.86420 | -11.87520 | H | -4.92000 | -3.91570 | -10.09330 |
| H | -7.74860 | 1.95550 | -9.67420 | H | -3.31880 | -4.62320 | -9.94260 |
| C | -6.45620 | 2.84150 | -12.37190 | H | -2.13960 | -3.68240 | -6.83950 |
| H | -8.54170 | 2.29730 | -11.93420 | H | -2.20650 | -5.41260 | -7.04080 |
| H | -7.54760 | 0.98380 | -12.51900 | H | -2.97320 | -4.67180 | -5.64870 |
| H | -5.46350 | 2.47400 | -12.11140 | H | -3.29880 | 2.72130 | -8.09910 |
| C | -6.59920 | 4.28900 | -11.90000 | C | -6.44940 | 6.30940 | -10.47730 |
| H | -6.45770 | 2.84300 | -13.46150 | H | -7.48690 | 6.61570 | -10.60930 |
| C | -6.30670 | 4.81320 | -10.68440 | H | -5.83650 | 6.85100 | -11.19860 |
| O | -6.96350 | 5.14590 | -12.90130 | H | -6.13050 | 6.60330 | -9.47710 |
| C | -5.86980 | 4.02460 | -9.54330 | H | -0.44610 | -1.05790 | -6.87080 |
| C | -4.77150 | 3.24510 | -9.49260 | C | -9.93540 | 7.02000 | -15.27740 |
| H | -6.50810 | 4.06240 | -8.67380 | H | -10.00720 | 7.95470 | -15.83420 |
| H | -4.12640 | 3.20520 | -10.35830 | H | -10.73610 | 7.01860 | -14.53720 |
| Si | -8.48200 | 5.22190 | -13.64720 | H | -10.13410 | 6.20780 | -15.97720 |
| C | -8.70660 | 3.77570 | -14.84280 | C | -7.45640 | 6.86630 | -15.69070 |
| C | -9.82540 | 5.19690 | -12.31910 | H | -7.44180 | 7.80250 | -16.24930 |
| C | -8.55520 | 6.86890 | -14.61420 | H | -7.60150 | 6.05850 | -16.40860 |
| H | -10.82050 | 5.24480 | -12.75820 | H | -6.46890 | 6.73280 | -15.24580 |
| H | -9.72370 | 6.04380 | -11.64260 | C | -8.31670 | 8.03350 | -13.63750 |
| H | -9.77360 | 4.29370 | -11.71460 | H | -8.32400 | 8.99450 | -14.15230 |
| H | -9.62230 | 3.87800 | -15.42250 | H | -7.35250 | 7.93660 | -13.13610 |
| H | -8.75860 | 2.82250 | -14.32120 | H | -9.08350 | 8.07080 | -12.86330 |
| H | -7.87770 | 3.71850 | -15.54700 | C | -0.40660 | 1.03680 | -7.23800 |
| C | -4.69780 | 3.58260 | -6.20000 | C | 0.95260 | 3.37670 | -8.05270 |
| O | -3.62190 | 4.17630 | -6.19840 | C | -0.86010 | 2.30600 | -6.82230 |
| C | -5.70630 | 3.76750 | -5.07860 | C | 0.75560 | 0.94580 | -8.03490 |
| H | -5.30700 | 4.43790 | -4.31770 | C | 1.42970 | 2.11190 | -8.44560 |
| H | -5.93400 | 2.80880 | -4.61370 | C | -0.19010 | 3.47240 | -7.23610 |
| H | -6.62870 | 4.19580 | -5.46980 | H | -1.72140 | 2.40150 | -6.17950 |
| H | -5.76300 | 0.04980 | -10.98880 | H | 1.13140 | -0.01950 | -8.34550 |
| C | -3.98110 | -1.37260 | -5.14020 | H | 2.31240 | 2.03470 | -9.06410 |
| H | -5.42050 | -0.09040 | -5.98540 | H | -0.55400 | 4.44020 | -6.92030 |
| C | -5.60750 | -3.15790 | -6.92080 | H | 1.46800 | 4.27230 | -8.36820 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.32330 | -0.96300 | -9.83380 | H | -3.50645 | -1.88188 | -1.28584 |
| O | -0.75700 | -1.96870 | -9.39680 | H | -5.00249 | -2.66380 | 0.81710 |
| C | -0.90730 | -0.46930 | -11.19650 | C | -4.40526 | -0.61739 | 0.88259 |
| C | -0.02580 | 0.40130 | -13.73940 | H | -3.53426 | -2.40732 | 1.72446 |
| C | -0.51480 | 0.87510 | -11.39720 | C | -3.56192 | 0.36583 | 1.29127 |
| C | -0.82110 | -1.37910 | -12.27330 | O | -5.61534 | -0.25477 | 0.34919 |
| C | -0.38980 | -0.94450 | -13.54230 | C | -2.20193 | 0.02255 | 1.69918 |
| C | -0.08480 | 1.31040 | -12.66590 | C | -1.12334 | 0.80678 | 1.55510 |
| H | -0.55110 | 1.57920 | -10.57770 | H | -2.03292 | -0.98555 | 2.06066 |
| H | -1.08760 | -2.41590 | -12.12250 | H | -1.21938 | 1.80844 | 1.14586 |
| H | -0.33460 | -1.64490 | -14.36320 | Si | -7.14149 | -0.95610 | 0.16718 |
| H | 0.20030 | 2.34200 | -12.81400 | C | -7.10890 | -2.24845 | -1.21321 |
| H | 0.30410 | 0.73520 | -14.71250 | C | -7.69034 | -1.75682 | 1.79052 |
| | | | | C | -8.27294 | 0.51270 | -0.30784 |

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Compound **5.18**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -2761.47221954 hartree.
Free Energy: -2760.601636 hartree.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.26295 | -1.46153 | 0.15851 | H | -8.73821 | -2.07627 | 1.73319 |
| C | 2.59288 | -0.16944 | 0.73386 | H | -7.60048 | -1.05929 | 2.63072 |
| C | 1.05953 | -0.06960 | 0.42483 | H | -7.09331 | -2.64384 | 2.03139 |
| C | 3.21544 | 1.15840 | 0.21533 | H | -8.11080 | -2.65897 | -1.38883 |
| H | 2.74150 | -0.21079 | 1.81623 | H | -6.45013 | -3.08983 | -0.97099 |
| H | 4.05851 | 0.97055 | -0.45090 | H | -6.75695 | -1.81631 | -2.15678 |
| C | 3.68098 | 2.13321 | 1.32884 | C | 0.88000 | -0.66849 | 3.85251 |
| C | 0.54813 | -1.40636 | -0.24973 | O | 1.42822 | 0.33895 | 4.24535 |
| C | 0.94984 | 1.08736 | -0.58463 | C | 0.70536 | -1.93231 | 4.66104 |
| C | 0.29517 | 0.34105 | 1.74216 | H | -0.35481 | -2.06915 | 4.90125 |
| H | 0.71808 | -2.18228 | 0.51135 | H | 1.27993 | -1.85624 | 5.58477 |
| C | 1.45467 | -1.67891 | -1.43554 | H | 1.02653 | -2.80508 | 4.08474 |
| C | -0.91397 | -1.47876 | -0.63017 | H | -1.28284 | -0.70459 | -1.29825 |
| C | 2.78850 | -1.71215 | -1.27267 | C | 4.77812 | -1.49303 | 0.39535 |
| O | 0.33302 | -0.81566 | 2.62074 | H | 2.84792 | -2.27748 | 0.77250 |
| O | -0.01935 | 1.34347 | -1.27214 | C | 3.74366 | -2.01292 | -2.40279 |
| N | 2.15600 | 1.79651 | -0.59291 | H | 0.99433 | -1.83137 | -2.40920 |
| H | 2.86781 | 2.26957 | 2.05096 | H | 5.31805 | -0.72870 | -0.17167 |
| C | -1.73929 | -2.42726 | -0.18039 | H | 5.19110 | -2.46635 | 0.11454 |
| C | -3.22291 | -2.51007 | -0.43383 | H | 5.00232 | -1.32651 | 1.45380 |
| H | -1.34863 | -3.17538 | 0.51510 | Si | 4.00441 | -3.87209 | -2.80499 |
| C | -4.06732 | -2.09599 | 0.81870 | H | 4.72297 | -1.55114 | -2.23231 |
| H | -3.49002 | -3.54364 | -0.69619 | H | 3.35845 | -1.56844 | -3.33106 |
| | | | | C | 4.55114 | -4.86655 | -1.28592 |
| | | | | C | 2.38335 | -4.59822 | -3.46079 |
| | | | | C | 5.34276 | -3.98914 | -4.14325 |
| | | | | H | 5.53832 | -4.55751 | -0.92269 |
| | | | | H | 4.61412 | -5.93394 | -1.53223 |
| | | | | H | 3.84154 | -4.76357 | -0.45643 |
| | | | | H | 1.57630 | -4.50281 | -2.72562 |
| | | | | H | 2.49797 | -5.66391 | -3.69425 |
| | | | | H | 2.05698 | -4.09290 | -4.37802 |
| | | | | H | 5.05891 | -3.43143 | -5.04396 |
| | | | | H | 5.51605 | -5.03033 | -4.44170 |

| | | | |
|---|---|---|---|
| H | 6.29915 | -3.58339 | -3.79140 |
| H | 0.87723 | 1.13038 | 2.22562 |
| C | -3.92883 | 1.82542 | 1.17478 |
| H | -5.00743 | 1.95947 | 1.08180 |
| H | -3.46185 | 2.28219 | 0.29068 |
| H | -3.57741 | 2.38401 | 2.05026 |
| H | 3.86326 | 3.10512 | 0.85735 |
| C | -8.37883 | 1.50812 | 0.86733 |
| H | -9.02023 | 2.35750 | 0.59080 |
| H | -7.40018 | 1.91292 | 1.14821 |
| H | -8.81884 | 1.04521 | 1.75896 |
| C | -9.68631 | -0.01008 | -0.64832 |
| H | -10.34729 | 0.82813 | -0.91091 |
| H | -10.15016 | -0.53322 | 0.19755 |
| H | -9.67757 | -0.69622 | -1.50353 |
| C | -7.69525 | 1.24531 | -1.53786 |
| H | -8.34303 | 2.08878 | -1.81807 |
| H | -7.62403 | 0.58699 | -2.41248 |
| H | -6.69502 | 1.64382 | -1.33801 |
| C | 4.93787 | 1.68861 | 2.04445 |
| C | 7.29286 | 0.84398 | 3.33186 |
| C | 4.88658 | 1.11931 | 3.32407 |
| C | 6.18732 | 1.83758 | 1.42366 |
| C | 7.35525 | 1.41797 | 2.05946 |
| C | 6.05649 | 0.69870 | 3.96233 |
| H | 3.92713 | 1.01037 | 3.82478 |
| H | 6.23932 | 2.29159 | 0.43603 |
| H | 8.31508 | 1.54418 | 1.56494 |
| H | 5.99971 | 0.26313 | 4.95678 |
| H | 8.20280 | 0.51988 | 3.83019 |
| C | 2.54789 | 2.78632 | -1.52607 |
| O | 3.73527 | 2.90047 | -1.79990 |
| C | 1.53746 | 3.71957 | -2.10454 |
| C | -0.15084 | 5.65229 | -3.21778 |
| C | 0.43660 | 4.19520 | -1.38017 |
| C | 1.79780 | 4.23530 | -3.38207 |
| C | 0.94715 | 5.18441 | -3.94330 |
| C | -0.39740 | 5.16434 | -1.93236 |
| H | 0.24088 | 3.81996 | -0.38215 |
| H | 2.67165 | 3.88287 | -3.92020 |
| H | 1.14543 | 5.56610 | -4.94103 |
| H | -1.24294 | 5.53652 | -1.36068 |
| H | -0.81024 | 6.40011 | -3.65043 |

---

Compound **5.18**
This structure was assigned as incorrect.
B3LYP/6-31g(d)

Gas phase.

Electronic Energy: -2761.46967103 hartree.
Free Energy: -2760.598160 hartree.

| | | | |
|---|---|---|---|
| C | -1.54484 | -2.27927 | 0.61187 |
| C | -1.61501 | -1.13897 | -0.46275 |
| C | -0.68058 | 0.07226 | -0.13036 |
| C | -3.04553 | -0.54165 | -0.64005 |
| H | -1.31104 | -1.58726 | -1.41348 |
| H | -3.74652 | -1.01963 | 0.04548 |
| C | -3.62540 | -0.63686 | -2.07480 |
| C | 0.20336 | -0.25534 | 1.13966 |
| C | -1.64399 | 1.22034 | 0.20179 |
| C | 0.20345 | 0.57394 | -1.32594 |
| H | 0.79593 | -1.12935 | 0.82675 |
| C | -0.71329 | -0.70913 | 2.25439 |
| C | 1.22039 | 0.78271 | 1.56897 |
| C | -1.57992 | -1.71312 | 2.03378 |
| O | -0.61235 | 0.57445 | -2.54722 |
| O | -1.33480 | 2.26181 | 0.74748 |
| N | -2.92702 | 0.87758 | -0.23325 |
| H | -2.85701 | -0.30584 | -2.77687 |
| C | 2.51024 | 0.45080 | 1.69317 |
| C | 3.68710 | 1.35591 | 1.93303 |
| H | 2.78336 | -0.58606 | 1.49465 |
| C | 4.48867 | 1.65320 | 0.61840 |
| H | 4.36625 | 0.89265 | 2.66121 |
| H | 3.36889 | 2.31758 | 2.35360 |
| H | 3.91045 | 2.36814 | 0.02667 |
| C | 4.82571 | 0.43886 | -0.23321 |
| H | 5.41399 | 2.17176 | 0.89043 |
| C | 3.97045 | -0.13756 | -1.12415 |
| O | 6.02082 | -0.17629 | 0.01997 |
| C | 2.63392 | 0.42795 | -1.26775 |
| C | 1.47260 | -0.18566 | -1.56580 |
| H | 2.53982 | 1.47488 | -0.99809 |
| H | 1.41266 | -1.23901 | -1.83280 |
| Si | 7.57243 | 0.32349 | 0.47905 |
| C | 8.06947 | 1.86475 | -0.49423 |
| C | 7.61721 | 0.67722 | 2.33518 |
| C | 8.68258 | -1.17231 | 0.04353 |
| H | 8.63091 | 0.94636 | 2.65559 |
| H | 7.30654 | -0.19803 | 2.91704 |
| H | 6.95815 | 1.50830 | 2.61012 |
| H | 9.12464 | 2.11062 | -0.32261 |
| H | 7.48048 | 2.74170 | -0.20286 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 7.93294 | 1.71774 | -1.57134 | C | -4.12202 | -2.01340 | -2.45801 |
| C | -0.67126 | 1.72848 | -3.25967 | C | -5.06608 | -4.57378 | -3.15468 |
| O | -0.20865 | 2.78641 | -2.89079 | C | -5.33634 | -2.49498 | -1.94546 |
| C | -1.41344 | 1.52679 | -4.56139 | C | -3.39670 | -2.83216 | -3.33308 |
| H | -1.11008 | 0.59349 | -5.04328 | C | -3.86191 | -4.10322 | -3.67924 |
| H | -1.22008 | 2.37573 | -5.21868 | C | -5.80380 | -3.76338 | -2.28781 |
| H | -2.49062 | 1.46838 | -4.36835 | H | -5.91787 | -1.86328 | -1.27742 |
| H | 0.87094 | 1.79882 | 1.73832 | H | -2.46184 | -2.46737 | -3.75351 |
| C | -2.50535 | -3.43852 | 0.31933 | H | -3.28546 | -4.72203 | -4.36231 |
| H | -0.53311 | -2.70140 | 0.48657 | H | -6.74828 | -4.11778 | -1.88285 |
| C | -2.41600 | -2.31468 | 3.14197 | H | -5.43175 | -5.56103 | -3.42436 |
| H | -0.60065 | -0.25319 | 3.23522 | C | -4.11337 | 1.60790 | 0.00410 |
| H | -3.55637 | -3.17503 | 0.46876 | O | -5.16834 | 0.99427 | 0.12471 |
| H | -2.28260 | -4.29263 | 0.96773 | C | -4.09366 | 3.09971 | 0.02535 |
| H | -2.39676 | -3.77488 | -0.71630 | C | -4.33218 | 5.88759 | -0.00586 |
| Si | -4.05013 | -1.47586 | 3.70978 | C | -3.20348 | 3.87409 | -0.73290 |
| H | -1.80662 | -2.33396 | 4.05677 | C | -5.11271 | 3.73323 | 0.75304 |
| H | -2.65210 | -3.36409 | 2.92897 | C | -5.22198 | 5.12092 | 0.75028 |
| C | -3.74372 | 0.35375 | 4.08498 | C | -3.33162 | 5.26124 | -0.75226 |
| C | -5.46473 | -1.66566 | 2.46549 | H | -2.41392 | 3.40838 | -1.31083 |
| C | -4.54143 | -2.37252 | 5.30999 | H | -5.81149 | 3.12093 | 1.31324 |
| H | -4.67314 | 0.84999 | 4.39019 | H | -6.00393 | 5.60352 | 1.33013 |
| H | -3.35112 | 0.88953 | 3.21363 | H | -2.64280 | 5.85287 | -1.34846 |
| H | -3.02049 | 0.47923 | 4.90023 | H | -4.42014 | 6.97094 | -0.01607 |
| H | -5.53910 | -2.69293 | 2.08767 | --- | | | |
| H | -5.37202 | -0.98678 | 1.61121 | | | | |
| H | -6.41839 | -1.43132 | 2.95608 | Compound **5.18** | | | |
| H | -4.72527 | -3.43968 | 5.13339 | This structure was assigned as incorrect. | | | |
| H | -5.45993 | -1.94783 | 5.73342 | B3LYP/6-31g(d) | | | |
| H | -3.75904 | -2.29402 | 6.07475 | SMD implicit solvation in chloroform was used. | | | |
| H | 0.45497 | 1.61422 | -1.11591 | | | | |
| C | 4.29303 | -1.42453 | -1.84149 | | | | |
| H | 4.07180 | -1.34048 | -2.91257 | Electronic Energy: -2761.51111467 hartree. | | | |
| H | 3.68429 | -2.25490 | -1.45571 | | | | |
| H | 5.34152 | -1.69921 | -1.72029 | Free Energy: -2760.638520 hartree. | | | |
| H | -4.46311 | 0.06536 | -2.13862 | | | | |
| C | 10.11752 | -0.92240 | 0.55982 | C | -1.54762 | -2.28012 | 0.51927 |
| H | 10.76756 | -1.76814 | 0.29412 | C | -1.62443 | -1.08553 | -0.49741 |
| H | 10.15176 | -0.81832 | 1.65092 | C | -0.71743 | 0.12522 | -0.08960 |
| H | 10.56598 | -0.02160 | 0.12183 | C | -3.06447 | -0.50968 | -0.66446 |
| C | 8.73183 | -1.37327 | -1.48654 | H | -1.29725 | -1.47974 | -1.46373 |
| H | 9.35379 | -2.24503 | -1.73602 | H | -3.76906 | -1.05135 | -0.03259 |
| H | 9.16539 | -0.50691 | -2.00054 | C | -3.61157 | -0.49828 | -2.11576 |
| H | 7.73575 | -1.54816 | -1.90834 | C | 0.15185 | -0.26034 | 1.17557 |
| C | 8.12671 | -2.45318 | 0.70253 | C | -1.70573 | 1.23848 | 0.27738 |
| H | 8.76478 | -3.31468 | 0.45793 | C | 0.18366 | 0.70592 | -1.23230 |
| H | 7.11259 | -2.67909 | 0.35629 | H | 0.74798 | -1.11437 | 0.81981 |
| H | 8.09639 | -2.37183 | 1.79610 | C | -0.77196 | -0.78243 | 2.25454 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.16925 | 0.74946 | 1.66730 | C | -3.87553 | 0.05814 | 4.17576 |
| C | -1.61142 | -1.79472 | 1.97017 | C | -5.50391 | -1.89563 | 2.40459 |
| O | -0.65716 | 0.83141 | -2.42935 | C | -4.55423 | -2.77656 | 5.18802 |
| O | -1.41510 | 2.27449 | 0.84971 | H | -4.82540 | 0.47134 | 4.54051 |
| N | -2.98369 | 0.87966 | -0.15215 | H | -3.54171 | 0.69166 | 3.34576 |
| H | -2.84774 | -0.06654 | -2.76577 | H | -3.14269 | 0.16223 | 4.98612 |
| C | 2.45896 | 0.40425 | 1.76589 | H | -5.57703 | -2.90639 | 1.98340 |
| C | 3.64864 | 1.27463 | 2.06141 | H | -5.40954 | -1.18253 | 1.57811 |
| H | 2.71873 | -0.62203 | 1.50432 | H | -6.46217 | -1.68369 | 2.89877 |
| C | 4.46687 | 1.63075 | 0.77152 | H | -4.70026 | -3.83523 | 4.93586 |
| H | 4.31341 | 0.75745 | 2.76619 | H | -5.48787 | -2.41863 | 5.64155 |
| H | 3.34631 | 2.21810 | 2.53175 | H | -3.77588 | -2.72811 | 5.96057 |
| H | 3.90673 | 2.38739 | 0.21565 | H | 0.45610 | 1.71883 | -0.93260 |
| C | 4.79504 | 0.46126 | -0.14356 | C | 4.25846 | -1.30176 | -1.86194 |
| H | 5.39625 | 2.11630 | 1.08499 | H | 3.92361 | -1.20402 | -2.90185 |
| C | 3.94172 | -0.05325 | -1.07618 | H | 3.74726 | -2.18204 | -1.44478 |
| O | 5.97633 | -0.18669 | 0.08586 | H | 5.32903 | -1.51621 | -1.86229 |
| C | 2.61043 | 0.52973 | -1.18645 | H | -4.47911 | 0.17012 | -2.13454 |
| C | 1.44280 | -0.05262 | -1.52571 | C | 10.08113 | -0.96137 | 0.54414 |
| H | 2.52655 | 1.55915 | -0.85438 | H | 10.73405 | -1.78808 | 0.22793 |
| H | 1.36827 | -1.08785 | -1.85365 | H | 10.11972 | -0.91989 | 1.63939 |
| Si | 7.54582 | 0.29725 | 0.52846 | H | 10.52613 | -0.03496 | 0.15836 |
| C | 8.00900 | 1.86474 | -0.41316 | C | 8.69034 | -1.31541 | -1.51614 |
| C | 7.62762 | 0.59187 | 2.39089 | H | 9.30691 | -2.17820 | -1.80888 |
| C | 8.64502 | -1.18548 | 0.02091 | H | 9.12722 | -0.42822 | -1.99116 |
| H | 8.65584 | 0.81330 | 2.70419 | H | 7.69307 | -1.46626 | -1.94650 |
| H | 7.29100 | -0.28462 | 2.95759 | C | 8.08939 | -2.49306 | 0.62365 |
| H | 7.00846 | 1.44326 | 2.69725 | H | 8.72828 | -3.34479 | 0.34636 |
| H | 9.07941 | 2.08352 | -0.30758 | H | 7.07683 | -2.70952 | 0.26514 |
| H | 7.46305 | 2.74089 | -0.04318 | H | 8.05441 | -2.45890 | 1.72004 |
| H | 7.79454 | 1.77106 | -1.48434 | C | -4.03921 | -1.85153 | -2.64168 |
| C | -0.39201 | 1.87005 | -3.26116 | C | -4.86025 | -4.36602 | -3.61725 |
| O | 0.42945 | 2.73267 | -3.02779 | C | -5.25103 | -2.42463 | -2.22497 |
| C | -1.25299 | 1.80876 | -4.49793 | C | -3.25206 | -2.55718 | -3.56256 |
| H | -1.11703 | 0.84909 | -5.00796 | C | -3.65679 | -3.80441 | -4.04739 |
| H | -0.98384 | 2.62536 | -5.16983 | C | -5.65811 | -3.67003 | -2.70453 |
| H | -2.31154 | 1.89332 | -4.22881 | H | -5.88212 | -1.88336 | -1.52348 |
| H | 0.82785 | 1.75577 | 1.90226 | H | -2.31757 | -2.12174 | -3.91016 |
| C | -2.48276 | -3.43693 | 0.14877 | H | -3.03342 | -4.33326 | -4.76422 |
| H | -0.52819 | -2.67851 | 0.38614 | H | -6.60182 | -4.09434 | -2.37073 |
| C | -2.43521 | -2.48474 | 3.03627 | H | -5.17866 | -5.33450 | -3.99434 |
| H | -0.67869 | -0.37827 | 3.26045 | C | -4.17751 | 1.58054 | 0.11024 |
| H | -3.54176 | -3.20072 | 0.29033 | O | -5.22903 | 0.95553 | 0.20741 |
| H | -2.25829 | -4.32200 | 0.75394 | C | -4.17071 | 3.07090 | 0.18512 |
| H | -2.34227 | -3.71794 | -0.90002 | C | -4.41161 | 5.85776 | 0.23446 |
| Si | -4.09538 | -1.74917 | 3.66011 | C | -3.35094 | 3.86361 | -0.63148 |
| H | -1.82734 | -2.54609 | 3.95060 | C | -5.12357 | 3.68379 | 1.01226 |
| H | -2.63860 | -3.52585 | 2.75754 | C | -5.23149 | 5.07245 | 1.04912 |

| | | | |
|---|---|---|---|
| C | -3.47949 | 5.25076 | -0.61187 |
| H | -2.62452 | 3.39927 | -1.28989 |
| H | -5.76960 | 3.06277 | 1.62478 |
| H | -5.95886 | 5.54106 | 1.70633 |
| H | -2.84898 | 5.85856 | -1.25488 |
| H | -4.50104 | 6.94071 | 0.25573 |

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Compound **5.18**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in chloroform was used.

Electronic Energy: -2760.51506818 hartree.
Free Energy: -2759.629532 hartree.

| | | | |
|---|---|---|---|
| C | 3.16456 | -0.35452 | -1.74859 |
| C | 2.59792 | 0.14126 | -0.40586 |
| C | 1.06177 | -0.08482 | -0.28291 |
| C | 2.81945 | 1.66127 | -0.25029 |
| H | 3.11578 | -0.40381 | 0.38876 |
| H | 3.51733 | 2.00905 | -1.01873 |
| C | 3.36811 | 2.15165 | 1.09866 |
| C | 0.56282 | -1.45057 | -0.88610 |
| C | 0.55987 | 1.23212 | -0.90502 |
| C | 0.67305 | -0.02524 | 1.23420 |
| H | 0.23062 | -2.04059 | -0.02280 |
| C | 1.64943 | -2.26933 | -1.54344 |
| C | -0.64997 | -1.34719 | -1.78906 |
| C | 2.84583 | -1.82013 | -1.93023 |
| O | 1.43659 | -1.08630 | 1.85107 |
| O | -0.42690 | 1.44431 | -1.57320 |
| N | 1.49633 | 2.21658 | -0.56830 |
| H | 2.71512 | 1.86140 | 1.92730 |
| C | -1.83077 | -1.86773 | -1.45429 |
| C | -3.13686 | -1.52111 | -2.11211 |
| H | -1.90172 | -2.42225 | -0.51789 |
| C | -3.75303 | -0.29103 | -1.39122 |
| H | -3.84329 | -2.35846 | -2.07168 |
| H | -2.98522 | -1.25792 | -3.16487 |
| H | -3.05960 | 0.54778 | -1.49514 |
| C | -4.07114 | -0.54635 | 0.06589 |
| H | -4.67153 | 0.00154 | -1.91022 |
| C | -3.21884 | -0.37012 | 1.10425 |
| O | -5.28146 | -1.13118 | 0.31113 |
| C | -1.83309 | 0.00717 | 0.82557 |
| C | -0.77593 | -0.24708 | 1.60925 |
| H | -1.65128 | 0.43999 | -0.14725 |
| H | -0.90614 | -0.69146 | 2.59555 |
| Si | -6.80985 | -0.74206 | -0.30332 |
| C | -7.01094 | 1.12108 | -0.26041 |
| C | -7.02807 | -1.41453 | -2.04445 |
| C | -8.01659 | -1.61171 | 0.86504 |
| H | -8.09404 | -1.45072 | -2.30182 |
| H | -6.63685 | -2.43486 | -2.12390 |
| H | -6.53399 | -0.80362 | -2.80695 |
| H | -7.95290 | 1.42610 | -0.73022 |
| H | -6.19778 | 1.62271 | -0.79795 |
| H | -7.00671 | 1.49942 | 0.76805 |
| C | 1.93798 | -0.85926 | 3.07751 |
| O | 1.74149 | 0.15973 | 3.70001 |
| C | 2.78234 | -2.01312 | 3.53799 |
| H | 3.04313 | -1.87705 | 4.58739 |
| H | 3.69666 | -2.04754 | 2.93515 |
| H | 2.24991 | -2.95662 | 3.39563 |
| H | -0.54733 | -0.76806 | -2.70585 |
| C | 2.67015 | 0.41770 | -2.98365 |
| H | 4.25467 | -0.22622 | -1.68691 |
| C | 3.91103 | -2.69915 | -2.51610 |
| H | 1.38704 | -3.31554 | -1.70467 |
| H | 2.91287 | 1.48557 | -2.94601 |
| H | 1.58669 | 0.31246 | -3.11047 |
| H | 3.13979 | 0.00739 | -3.88395 |
| Si | 5.09474 | -3.35035 | -1.17482 |
| H | 4.49071 | -2.15734 | -3.27628 |
| H | 3.46769 | -3.57401 | -3.00968 |
| C | 5.97339 | -1.93576 | -0.29238 |
| C | 4.09553 | -4.33556 | 0.07943 |
| C | 6.37114 | -4.45425 | -2.01055 |
| H | 6.67583 | -2.33565 | 0.44937 |
| H | 5.27670 | -1.27631 | 0.24084 |
| H | 6.55225 | -1.31975 | -0.99021 |
| H | 4.74651 | -4.75324 | 0.85648 |
| H | 3.34940 | -3.69990 | 0.57069 |
| H | 3.56289 | -5.16961 | -0.39233 |
| H | 5.89287 | -5.29455 | -2.52674 |
| H | 7.07951 | -4.86950 | -1.28451 |
| H | 6.94942 | -3.89461 | -2.75475 |
| H | 1.02610 | 0.91834 | 1.65742 |
| C | -3.61008 | -0.73559 | 2.51068 |
| H | -3.31476 | -1.76335 | 2.76006 |
| H | -4.69042 | -0.66063 | 2.64933 |
| H | -3.12145 | -0.07154 | 3.23132 |
| H | 3.39097 | 3.24754 | 1.06722 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -7.59837 | -1.39831 | 2.32484 | C | -2.57766 | -0.89801 | 0.11785 |
| H | -8.34411 | -1.83967 | 3.00116 | C | -1.04896 | -0.58328 | -0.03665 |
| H | -7.51572 | -0.33394 | 2.57929 | C | -3.22261 | -0.46878 | -1.22991 |
| H | -6.63358 | -1.87206 | 2.53382 | H | -2.71671 | -1.97662 | 0.23029 |
| C | -8.04077 | -3.11722 | 0.56553 | H | -4.16303 | 0.06565 | -1.08526 |
| H | -8.70716 | -3.63355 | 1.27086 | C | -3.48968 | -1.65367 | -2.19838 |
| H | -7.04569 | -3.56831 | 0.66253 | C | -0.53547 | 0.24983 | 1.21572 |
| H | -8.40913 | -3.32540 | -0.44598 | C | -0.96661 | 0.31398 | -1.28550 |
| C | -9.42124 | -1.02892 | 0.65001 | C | -0.25483 | -1.92257 | -0.27696 |
| H | -9.75146 | -1.11391 | -0.39325 | H | -0.64580 | -0.44242 | 2.06300 |
| H | -9.46898 | 0.02972 | 0.93161 | C | -1.48107 | 1.41813 | 1.42410 |
| H | -10.15364 | -1.56733 | 1.26752 | C | 0.91151 | 0.68863 | 1.19353 |
| C | 4.75997 | 1.61767 | 1.35049 | C | -2.80692 | 1.21091 | 1.51387 |
| C | 7.34092 | 0.60864 | 1.81060 | O | -0.27690 | -2.63772 | 0.98872 |
| C | 5.81241 | 1.92239 | 0.47904 | O | 0.04446 | 0.80004 | -1.75425 |
| C | 5.02285 | 0.80586 | 2.45758 | N | -2.25673 | 0.49240 | -1.79573 |
| C | 6.30357 | 0.30475 | 2.68831 | H | -2.58954 | -2.27487 | -2.27110 |
| C | 7.09180 | 1.42225 | 0.70590 | C | 1.77026 | 0.40814 | 2.17694 |
| H | 5.63223 | 2.57291 | -0.37435 | C | 3.24765 | 0.70475 | 2.18605 |
| H | 4.21883 | 0.58661 | 3.15700 | H | 1.41540 | -0.17969 | 3.02810 |
| H | 6.49014 | -0.31935 | 3.55803 | C | 4.11124 | -0.58293 | 1.96152 |
| H | 7.89798 | 1.67251 | 0.02215 | H | 3.52614 | 1.13582 | 3.15824 |
| H | 8.33904 | 0.21852 | 1.98691 | H | 3.49955 | 1.44939 | 1.42254 |
| C | 1.36448 | 3.58386 | -0.85189 | H | 5.04810 | -0.48204 | 2.51735 |
| O | 2.35334 | 4.24058 | -1.11877 | C | 4.44184 | -0.86956 | 0.50749 |
| C | 0.01579 | 4.20375 | -0.70552 | H | 3.59332 | -1.43875 | 2.41044 |
| C | -2.41443 | 5.51724 | -0.36525 | C | 3.59658 | -1.43120 | -0.39498 |
| C | -0.92369 | 3.70971 | 0.20442 | O | 5.64711 | -0.39159 | 0.05888 |
| C | -0.25561 | 5.36611 | -1.42898 | C | 2.24277 | -1.79837 | 0.01606 |
| C | -1.47516 | 6.01557 | -1.26661 | C | 1.15843 | -1.77661 | -0.77323 |
| C | -2.13503 | 4.36834 | 0.37480 | H | 2.08603 | -2.01369 | 1.06737 |
| H | -0.70640 | 2.81926 | 0.78873 | H | 1.24073 | -1.50969 | -1.82198 |
| H | 0.49245 | 5.74800 | -2.11699 | Si | 7.16950 | -0.07468 | 0.71763 |
| H | -1.69193 | 6.91209 | -1.83917 | C | 7.13503 | 1.54106 | 1.69835 |
| H | -2.86041 | 3.98442 | 1.08548 | C | 7.72425 | -1.49952 | 1.83157 |
| H | -3.36454 | 6.02684 | -0.23456 | C | 8.30544 | 0.08579 | -0.81246 |
| ---------- | | | | H | 8.78592 | -1.39759 | 2.08846 |
| | | | | H | 7.59505 | -2.46800 | 1.33554 |
| Compound **5.18** | | | | H | 7.16483 | -1.53276 | 2.77331 |
| This structure was assigned as correct. | | | | H | 8.12878 | 1.77191 | 2.10060 |
| B3LYP/6-31g(d) | | | | H | 6.44349 | 1.49263 | 2.54680 |
| Gas phase. | | | | H | 6.82661 | 2.38394 | 1.06962 |
| | | | | C | -0.71749 | -3.92028 | 0.99060 |
| Electronic Energy: -2761.47170573 hartree. | | | | O | -1.18904 | -4.48628 | 0.02837 |
| | | | | C | -0.52999 | -4.54194 | 2.35452 |
| Free Energy: -2760.603167 hartree. | | | | H | 0.53770 | -4.71265 | 2.53258 |
| | | | | H | -1.05905 | -5.49465 | 2.39579 |
| C | -3.23519 | -0.24962 | 1.38004 | H | -0.89136 | -3.87108 | 3.13930 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 1.24537 | 1.24163 | 0.31834 | H | -3.50238 | -4.12441 | -0.97527 |
| C | -4.74027 | -0.53892 | 1.45876 | H | -5.46382 | -5.45389 | -0.26744 |
| H | -2.78248 | -0.78707 | 2.22929 | H | -8.08680 | -2.40686 | -1.79832 |
| C | -3.79650 | 2.32164 | 1.76967 | H | -7.76700 | -4.60101 | -0.66790 |
| H | -1.05314 | 2.41505 | 1.51117 | C | -2.67685 | 1.36918 | -2.81312 |
| H | -5.31657 | -0.03914 | 0.67383 | O | -3.74170 | 1.15548 | -3.37968 |
| H | -5.14770 | -0.21794 | 2.42215 | C | -1.88063 | 2.59316 | -3.13463 |
| H | -4.92472 | -1.61377 | 1.35880 | C | -0.63819 | 4.99873 | -3.83795 |
| Si | -4.00133 | 2.85418 | 3.60367 | C | -1.25711 | 3.37623 | -2.15441 |
| H | -4.78537 | 2.07450 | 1.36707 | C | -1.89756 | 3.03547 | -4.46451 |
| H | -3.47359 | 3.22899 | 1.24051 | C | -1.26321 | 4.22427 | -4.81762 |
| C | -5.43511 | 4.09164 | 3.68703 | C | -0.64665 | 4.57800 | -2.50602 |
| C | -4.37613 | 1.38247 | 4.73734 | H | -1.26231 | 3.05498 | -1.11844 |
| C | -2.40404 | 3.69093 | 4.18190 | H | -2.41398 | 2.43869 | -5.20933 |
| H | -6.37845 | 3.63680 | 3.36105 | H | -1.26494 | 4.55112 | -5.85380 |
| H | -5.25142 | 4.96415 | 3.04829 | H | -0.17361 | 5.18589 | -1.73965 |
| H | -5.58270 | 4.45840 | 4.71025 | H | -0.15063 | 5.93112 | -4.11032 |
| H | -5.33491 | 0.90943 | 4.49495 | | | | |
| H | -4.42999 | 1.71102 | 5.78280 | | | | |
| H | -3.59716 | 0.61331 | 4.67618 | | | | |
| H | -1.54352 | 3.01842 | 4.09058 | | | | |
| H | -2.47834 | 3.99616 | 5.23284 | | | | |
| H | -2.18722 | 4.58999 | 3.59210 | | | | |
| H | -0.82619 | -2.52123 | -0.99072 | | | | |
| C | 3.95512 | -1.53757 | -1.85760 | | | | |
| H | 5.03083 | -1.44258 | -2.01195 | | | | |
| H | 3.46485 | -0.74779 | -2.44385 | | | | |
| H | 3.62199 | -2.49741 | -2.26953 | | | | |
| H | -3.67716 | -1.22870 | -3.18738 | | | | |
| C | 8.43261 | -1.27774 | -1.52589 | C | -3.08287 | -1.15322 | 1.68049 |
| H | 9.06680 | -1.18170 | -2.41896 | C | -2.48409 | -1.10259 | 0.24810 |
| H | 7.45923 | -1.66017 | -1.85292 | C | -0.95039 | -0.83376 | 0.23122 |
| H | 8.89169 | -2.03688 | -0.88104 | C | -3.10488 | -0.01129 | -0.65728 |
| C | 9.71255 | 0.55251 | -0.37622 | H | -2.68822 | -2.07742 | -0.20980 |
| H | 10.37593 | 0.62044 | -1.25029 | H | -3.89901 | 0.52196 | -0.12968 |
| H | 10.18187 | -0.14406 | 0.33026 | C | -3.67326 | -0.54541 | -1.98406 |
| H | 9.69327 | 1.54398 | 0.09237 | C | -0.35521 | -0.95158 | 1.67230 |
| C | 7.71850 | 1.11727 | -1.80068 | C | -0.82873 | 0.60503 | -0.26583 |
| H | 8.36253 | 1.20311 | -2.68788 | C | -0.29132 | -1.76302 | -0.83659 |
| H | 7.64583 | 2.11715 | -1.35500 | H | -0.57074 | -1.98526 | 1.98313 |
| H | 6.71781 | 0.82924 | -2.13899 | C | -1.14522 | -0.00104 | 2.54712 |
| C | -4.67318 | -2.49853 | -1.77785 | C | 1.13106 | -0.74645 | 1.82569 |
| C | -6.90517 | -4.01426 | -0.97519 | C | -2.48466 | -0.06184 | 2.55787 |
| C | -5.97734 | -2.03283 | -2.00678 | O | -0.31627 | -3.08756 | -0.28698 |
| C | -4.50472 | -3.73953 | -1.14844 | O | 0.12480 | 1.33695 | -0.12131 |
| C | -5.61345 | -4.49106 | -0.74951 | N | -2.01884 | 0.94695 | -0.90691 |
| C | -7.08415 | -2.78157 | -1.60821 | H | -2.92025 | -1.17334 | -2.47425 |
| H | -6.11904 | -1.07908 | -2.51099 | C | 1.95342 | -1.68176 | 2.29764 |

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Compound **5.18**

This structure was assigned as correct.

M06-2X/6-31g(d)

SMD implicit solvation in chloroform was used.

Electronic Energy: -2760.51820977 hartree.

Free Energy: -2759.634975 hartree.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.44667 | -1.54759 | 2.41927 | H | -2.62024 | 4.28322 | 1.40039 |
| H | 1.54511 | -2.66181 | 2.55946 | H | -1.81837 | 2.71110 | 1.20809 |
| C | 4.22424 | -2.40381 | 1.38047 | H | -5.00165 | 2.09511 | 0.50808 |
| H | 3.75892 | -1.86563 | 3.42212 | H | -5.68009 | 3.47326 | 1.36257 |
| H | 3.73017 | -0.49329 | 2.31535 | H | -6.09361 | 1.83935 | 1.89255 |
| H | 5.20366 | -2.67037 | 1.78968 | H | -0.93163 | -1.75090 | -1.72354 |
| C | 4.47659 | -1.69429 | 0.06611 | C | 3.86817 | -0.61263 | -2.10403 |
| H | 3.68618 | -3.34580 | 1.22024 | H | 4.94137 | -0.44832 | -2.21663 |
| C | 3.56780 | -1.47368 | -0.90690 | H | 3.38195 | 0.36801 | -2.01197 |
| O | 5.75814 | -1.22669 | -0.07825 | H | 3.48678 | -1.07510 | -3.02122 |
| C | 2.20068 | -1.96828 | -0.73278 | H | -3.88255 | 0.30827 | -2.63799 |
| C | 1.10836 | -1.37904 | -1.22381 | C | 9.07138 | -0.55539 | 0.08942 |
| H | 2.06042 | -2.82391 | -0.07809 | H | 9.99491 | -0.38922 | -0.48318 |
| H | 1.18389 | -0.48880 | -1.84458 | H | 8.73500 | -1.57858 | -0.11775 |
| Si | 6.40300 | 0.15977 | 0.63936 | H | 9.32994 | -0.49396 | 1.15324 |
| C | 5.18484 | 1.57051 | 0.43313 | C | 8.51955 | 1.88724 | 0.05647 |
| C | 6.76926 | -0.16356 | 2.45342 | H | 9.48235 | 2.08015 | -0.43716 |
| C | 8.01162 | 0.48321 | -0.30141 | H | 8.67855 | 2.00676 | 1.13570 |
| H | 7.43505 | 0.61115 | 2.85363 | H | 7.82095 | 2.66740 | -0.26898 |
| H | 7.26860 | -1.12963 | 2.58758 | C | 7.76186 | 0.40425 | -1.81259 |
| H | 5.86604 | -0.16176 | 3.07245 | H | 8.68328 | 0.63975 | -2.36394 |
| H | 5.43993 | 2.40820 | 1.09243 | H | 6.99468 | 1.11825 | -2.13778 |
| H | 4.16390 | 1.25604 | 0.68098 | H | 7.43908 | -0.59862 | -2.11286 |
| H | 5.17178 | 1.94576 | -0.59632 | C | -4.93893 | -1.33027 | -1.75037 |
| C | -1.01634 | -4.03739 | -0.94030 | C | -7.27885 | -2.75423 | -1.15233 |
| O | -1.65187 | -3.83095 | -1.94751 | C | -6.12246 | -0.65492 | -1.43319 |
| C | -0.90169 | -5.35727 | -0.23475 | C | -4.94434 | -2.72671 | -1.77654 |
| H | -1.47056 | -6.11323 | -0.77476 | C | -6.10886 | -3.43535 | -1.47950 |
| H | 0.14966 | -5.65147 | -0.17368 | C | -7.28415 | -1.35938 | -1.13308 |
| H | -1.28201 | -5.25969 | 0.78620 | H | -6.12470 | 0.43393 | -1.41662 |
| H | 1.52610 | 0.22463 | 1.52999 | H | -4.02880 | -3.25998 | -2.02545 |
| C | -4.60768 | -1.24755 | 1.68470 | H | -6.10024 | -4.52143 | -1.50447 |
| H | -2.71590 | -2.10624 | 2.09268 | H | -8.19495 | -0.82095 | -0.88719 |
| C | -3.32771 | 0.84184 | 3.41540 | H | -8.18476 | -3.30611 | -0.91928 |
| H | -0.60105 | 0.71833 | 3.15749 | C | -2.34572 | 2.21208 | -1.41666 |
| H | -5.09019 | -0.31315 | 1.37992 | O | -3.50872 | 2.57392 | -1.42470 |
| H | -4.97194 | -1.49728 | 2.68609 | C | -1.26710 | 3.05093 | -2.01159 |
| H | -4.94551 | -2.03517 | 1.00205 | C | 0.59368 | 4.70205 | -3.25535 |
| Si | -3.83297 | 2.53997 | 2.70573 | C | -0.22518 | 2.48998 | -2.75366 |
| H | -2.75781 | 1.09250 | 4.32063 | C | -1.38937 | 4.43732 | -1.91097 |
| H | -4.23634 | 0.33347 | 3.76030 | C | -0.44891 | 5.26205 | -2.51989 |
| C | -4.40079 | 3.56476 | 4.18549 | C | 0.69878 | 3.31671 | -3.38101 |
| C | -2.33225 | 3.36334 | 1.92257 | H | -0.15015 | 1.41073 | -2.85295 |
| C | -5.27981 | 2.46079 | 1.50052 | H | -2.22087 | 4.85779 | -1.35335 |
| H | -4.72802 | 4.56280 | 3.87157 | H | -0.53368 | 6.34037 | -2.42688 |
| H | -3.59768 | 3.69430 | 4.92000 | H | 1.50275 | 2.88113 | -3.96645 |
| H | -5.24477 | 3.08744 | 4.69751 | H | 1.32365 | 5.34601 | -3.73698 |
| H | -1.59872 | 3.63628 | 2.69104 | ---------- | | | |

Compound **5.19**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +46.593971 kJ.

| | | | |
|---|---|---|---|
| C | -4.15890 | -9.33960 | -2.74790 |
| C | -4.34230 | -7.87470 | -3.10950 |
| C | -3.57540 | -6.81650 | -2.75760 |
| C | -2.41870 | -6.80690 | -1.83270 |
| C | -1.16360 | -9.48140 | 0.34030 |
| H | -0.49360 | -9.53520 | 1.19920 |
| C | -2.43580 | -10.30870 | 0.65230 |
| H | -2.22370 | -10.95260 | 1.50670 |
| C | -2.91240 | -11.21150 | -0.50890 |
| H | -3.24080 | -9.66090 | 0.99550 |
| H | -2.71550 | -12.24850 | -0.23360 |
| H | -2.30700 | -11.05450 | -1.39990 |
| O | -1.62280 | -5.86990 | -1.78540 |
| H | -3.83760 | -5.85060 | -3.16250 |
| C | -1.40040 | -7.98890 | 0.01800 |
| O | -2.35460 | -7.88720 | -1.03010 |
| H | -0.45040 | -7.57380 | -0.32320 |
| C | -1.86260 | -7.18630 | 1.24870 |
| H | -0.60400 | -9.94120 | -0.47460 |
| C | -4.41070 | -11.08700 | -0.86170 |
| H | -4.66600 | -11.85720 | -1.59060 |
| H | -5.00390 | -11.31220 | 0.02550 |
| H | -1.93030 | -6.12280 | 1.01820 |
| H | -1.15780 | -7.29330 | 2.07310 |
| H | -2.84240 | -7.50670 | 1.60070 |
| C | -4.84170 | -9.71580 | -1.41940 |
| H | -4.65500 | -8.94790 | -0.66950 |
| H | -5.92240 | -9.71350 | -1.56630 |
| H | -5.18200 | -7.68050 | -3.76040 |
| H | -3.09140 | -9.54700 | -2.72740 |
| H | -4.55250 | -9.95410 | -3.55820 |

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Compound **5.19**
This structure was assigned as ambiguous.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +56.558006 kJ.

| | | | |
|---|---|---|---|
| C | -5.13730 | -8.72240 | -1.94800 |
| C | -4.43710 | -7.92690 | -3.04020 |
| C | -3.29330 | -7.20420 | -3.01680 |
| C | -2.31800 | -7.01670 | -1.91920 |
| C | -1.03000 | -9.32190 | 0.09670 |
| H | -0.10100 | -9.35850 | 0.66650 |
| C | -1.91890 | -10.49390 | 0.57990 |
| H | -1.41660 | -11.43250 | 0.34370 |
| C | -3.35600 | -10.54320 | 0.02850 |
| H | -1.97450 | -10.46100 | 1.66860 |
| H | -3.89370 | -9.66990 | 0.38880 |
| H | -3.87840 | -11.39040 | 0.47430 |
| O | -1.30660 | -6.33300 | -2.07330 |
| H | -3.01340 | -6.71400 | -3.93730 |
| C | -1.60420 | -7.88930 | 0.21490 |
| O | -2.60040 | -7.68940 | -0.78580 |
| H | -0.77310 | -7.20190 | 0.05110 |
| C | -2.17400 | -7.54540 | 1.59890 |
| H | -0.72780 | -9.49480 | -0.93660 |
| C | -3.46720 | -10.64980 | -1.50490 |
| H | -2.71160 | -10.04370 | -2.00170 |
| H | -3.25560 | -11.67790 | -1.80080 |
| H | -2.48760 | -6.50200 | 1.63470 |
| H | -1.42360 | -7.69090 | 2.37580 |
| H | -3.03970 | -8.15530 | 1.85200 |
| C | -4.85680 | -10.23850 | -2.02460 |
| H | -5.61800 | -10.77490 | -1.45630 |
| H | -4.97100 | -10.57210 | -3.05690 |
| H | -4.95900 | -7.95440 | -3.98550 |
| H | -6.20620 | -8.56210 | -2.09330 |
| H | -4.93810 | -8.31260 | -0.96080 |

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Compound **5.19**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -580.444126299 hartree.
Free Energy: -580.206896 hartree.

| | | | |
|---|---|---|---|
| C | -4.91455 | -8.77468 | -1.85156 |
| C | -4.11509 | -8.15471 | -2.96562 |
| C | -3.18612 | -7.19774 | -2.84825 |
| C | -2.81867 | -6.51016 | -1.56351 |
| C | -1.31838 | -9.27132 | 0.28136 |

| | | | |
|---|---|---|---|
| H | -0.93672 | -8.69062 | 1.13148 |
| C | -2.67398 | -9.88978 | 0.67183 |
| H | -2.59310 | -10.19895 | 1.72237 |
| C | -3.11991 | -11.13953 | -0.11630 |
| H | -3.44523 | -9.11264 | 0.65927 |
| H | -3.95256 | -11.60091 | 0.43450 |
| H | -2.29839 | -11.86967 | -0.07085 |
| O | -3.14178 | -5.36485 | -1.34908 |
| H | -2.74289 | -6.75720 | -3.73907 |
| C | -1.30144 | -8.34339 | -0.93580 |
| O | -2.13715 | -7.19933 | -0.60969 |
| H | -1.71796 | -8.84187 | -1.81281 |
| C | 0.10211 | -7.83398 | -1.25879 |
| H | -0.58784 | -10.07287 | 0.10214 |
| C | -3.55721 | -11.01718 | -1.59143 |
| H | -2.77113 | -10.55123 | -2.19895 |
| H | -3.64432 | -12.04349 | -1.97347 |
| H | 0.08393 | -7.15328 | -2.11700 |
| H | 0.76648 | -8.67066 | -1.50298 |
| H | 0.52071 | -7.29327 | -0.40341 |
| C | -4.90595 | -10.31891 | -1.85675 |
| H | -5.64243 | -10.67355 | -1.12243 |
| H | -5.27766 | -10.65043 | -2.83677 |
| H | -4.36788 | -8.49526 | -3.97132 |
| H | -5.95918 | -8.45022 | -1.97456 |
| H | -4.58942 | -8.37963 | -0.88555 |

---

Compound **5.19**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -580.212861749 hartree.
Free Energy: -579.970017 hartree.

| | | | |
|---|---|---|---|
| C | -5.17335 | -8.70734 | -1.91204 |
| C | -4.49650 | -7.90627 | -2.98641 |
| C | -3.29957 | -7.30493 | -2.99547 |
| C | -2.25251 | -7.29081 | -1.94598 |
| C | -1.03364 | -9.24945 | 0.09035 |
| H | -0.09049 | -9.27586 | 0.65036 |
| C | -1.90249 | -10.42802 | 0.54933 |
| H | -1.37793 | -11.35454 | 0.28071 |
| C | -3.32730 | -10.47085 | -0.01046 |
| H | -1.96163 | -10.42190 | 1.64531 |
| H | -3.87130 | -9.58498 | 0.33372 |
| H | -3.84858 | -11.33271 | 0.42671 |
| O | -1.10381 | -6.99758 | -2.20435 |
| H | -2.96212 | -6.81728 | -3.90557 |
| C | -1.62792 | -7.85105 | 0.27053 |
| O | -2.66997 | -7.63704 | -0.71678 |
| H | -0.84388 | -7.11584 | 0.07339 |
| C | -2.23732 | -7.58464 | 1.63329 |
| H | -0.75863 | -9.35789 | -0.96535 |
| C | -3.43339 | -10.56289 | -1.53473 |
| H | -2.70555 | -9.89952 | -2.01796 |
| H | -3.17544 | -11.58017 | -1.85499 |
| H | -2.58609 | -6.55011 | 1.69910 |
| H | -1.47815 | -7.74011 | 2.40677 |
| H | -3.08148 | -8.24626 | 1.84585 |
| C | -4.83947 | -10.21175 | -2.02964 |
| H | -5.57727 | -10.77671 | -1.44539 |
| H | -4.96213 | -10.52341 | -3.07417 |
| H | -5.05230 | -7.84641 | -3.92296 |
| H | -6.25462 | -8.57915 | -2.02950 |
| H | -4.90384 | -8.33805 | -0.92124 |

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Compound **5.19**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -580.473529068 hartree.
Free Energy: -580.234494 hartree.

| | | | |
|---|---|---|---|
| C | -5.17442 | -8.72504 | -1.94856 |
| C | -4.48489 | -7.90575 | -3.00438 |
| C | -3.31308 | -7.24391 | -2.98297 |
| C | -2.27506 | -7.16683 | -1.92959 |
| C | -1.03368 | -9.27918 | 0.11433 |
| H | -0.09752 | -9.31846 | 0.68842 |
| C | -1.91701 | -10.46061 | 0.56510 |
| H | -1.37853 | -11.38511 | 0.31183 |
| C | -3.34554 | -10.52804 | -0.00411 |
| H | -1.99001 | -10.45229 | 1.66118 |
| H | -3.89946 | -9.64921 | 0.34138 |
| H | -3.85252 | -11.39384 | 0.44576 |
| O | -1.16268 | -6.72269 | -2.16780 |
| H | -2.99368 | -6.73119 | -3.88677 |
| C | -1.59275 | -7.85576 | 0.27196 |

| | | | |
|---|---|---|---|
| O | -2.64983 | -7.64110 | -0.71998 |
| H | -0.79368 | -7.14893 | 0.03819 |
| C | -2.17868 | -7.52452 | 1.63663 |
| H | -0.74026 | -9.40140 | -0.93542 |
| C | -3.46248 | -10.63315 | -1.53488 |
| H | -2.71345 | -10.00141 | -2.02583 |
| H | -3.23884 | -11.66285 | -1.84639 |
| H | -2.50736 | -6.48022 | 1.66902 |
| H | -1.41282 | -7.66229 | 2.40876 |
| H | -3.03323 | -8.15984 | 1.88855 |
| C | -4.85773 | -10.24306 | -2.05238 |
| H | -5.62233 | -10.78858 | -1.48193 |
| H | -4.96926 | -10.56088 | -3.09770 |
| H | -5.01753 | -7.86410 | -3.95602 |
| H | -6.25551 | -8.59315 | -2.08317 |
| H | -4.92488 | -8.36012 | -0.95084 |

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Compound **5.19**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -580.460119784 hartree.
Free Energy: -580.220781 hartree.

| | | | |
|---|---|---|---|
| C | -5.17061 | -8.72234 | -1.95061 |
| C | -4.47717 | -7.90988 | -3.01059 |
| C | -3.30953 | -7.24314 | -2.98478 |
| C | -2.28030 | -7.15125 | -1.92216 |
| C | -1.03137 | -9.28327 | 0.11455 |
| H | -0.09570 | -9.32283 | 0.68967 |
| C | -1.91543 | -10.46570 | 0.56312 |
| H | -1.38074 | -11.39080 | 0.30512 |
| C | -3.34601 | -10.52787 | -0.00217 |
| H | -1.98516 | -10.46261 | 1.65943 |
| H | -3.89569 | -9.64601 | 0.34218 |
| H | -3.85599 | -11.39060 | 0.44973 |
| O | -1.17914 | -6.68025 | -2.14269 |
| H | -2.98210 | -6.73176 | -3.88593 |
| C | -1.59518 | -7.86074 | 0.26724 |
| O | -2.65327 | -7.65998 | -0.72060 |
| H | -0.79976 | -7.15280 | 0.02395 |
| C | -2.17855 | -7.52519 | 1.63351 |
| H | -0.73530 | -9.40267 | -0.93463 |
| C | -3.46578 | -10.63493 | -1.53261 |
| H | -2.71806 | -10.00425 | -2.02565 |
| H | -3.24412 | -11.66516 | -1.84306 |
| H | -2.52295 | -6.48644 | 1.65501 |
| H | -1.40899 | -7.64600 | 2.40455 |
| H | -3.02322 | -8.17070 | 1.89180 |
| C | -4.86167 | -10.24230 | -2.04672 |
| H | -5.62562 | -10.78246 | -1.47036 |
| H | -4.97846 | -10.56605 | -3.08964 |
| H | -5.00422 | -7.87835 | -3.96603 |
| H | -6.25176 | -8.58561 | -2.08290 |
| H | -4.91687 | -8.35159 | -0.95635 |

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Compound **5.19**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -580.209167372 hartree.
Free Energy: -579.967500 hartree.

| | | | |
|---|---|---|---|
| C | -4.24179 | -9.17150 | -3.34039 |
| C | -4.67141 | -7.80072 | -2.89599 |
| C | -3.95869 | -6.96768 | -2.13550 |
| C | -2.59475 | -7.32396 | -1.64082 |
| C | -1.96719 | -9.21200 | 1.17533 |
| H | -2.97534 | -8.98108 | 1.54114 |
| C | -1.95065 | -10.53619 | 0.39832 |
| H | -0.90410 | -10.83987 | 0.26603 |
| C | -2.61633 | -10.52897 | -0.98212 |
| H | -2.41753 | -11.30839 | 1.02366 |
| H | -2.45965 | -11.51525 | -1.44036 |
| H | -2.08431 | -9.81895 | -1.62568 |
| O | -1.61569 | -7.50199 | -2.32968 |
| H | -4.38044 | -6.03594 | -1.76759 |
| C | -1.47369 | -7.99331 | 0.39272 |
| O | -2.62337 | -7.45674 | -0.30809 |
| H | -0.72527 | -8.27931 | -0.35227 |
| C | -0.93238 | -6.88822 | 1.28211 |
| H | -1.33581 | -9.32973 | 2.06422 |
| C | -4.11760 | -10.23217 | -0.98094 |
| H | -4.62203 | -10.97766 | -0.35147 |
| H | -4.31157 | -9.25627 | -0.51970 |
| H | -0.66642 | -6.01093 | 0.68485 |
| H | -0.03694 | -7.23226 | 1.80827 |
| H | -1.68029 | -6.59263 | 2.02544 |
| C | -4.74405 | -10.27180 | -2.38065 |

| | | | |
|---|---|---|---|
| H | -5.83475 | -10.19167 | -2.29218 |
| H | -4.53752 | -11.24677 | -2.84069 |
| H | -5.68544 | -7.50210 | -3.16087 |
| H | -3.15253 | -9.21672 | -3.42773 |
| H | -4.64975 | -9.36611 | -4.33836 |

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Compound **5.19**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in diethyl ether was used.

Electronic Energy: -580.470362771 hartree.
Free Energy: -580.231946 hartree.

| | | | |
|---|---|---|---|
| C | -4.27693 | -9.16778 | -3.35752 |
| C | -4.67364 | -7.78884 | -2.89651 |
| C | -3.93724 | -6.95611 | -2.14869 |
| C | -2.57076 | -7.30580 | -1.65637 |
| C | -1.95678 | -9.18518 | 1.16245 |
| H | -2.96483 | -8.95439 | 1.52936 |
| C | -1.94369 | -10.52508 | 0.39541 |
| H | -0.89590 | -10.82658 | 0.25582 |
| C | -2.62998 | -10.58443 | -0.98245 |
| H | -2.38822 | -11.28495 | 1.05409 |
| H | -2.46708 | -11.59240 | -1.39138 |
| H | -2.10604 | -9.90636 | -1.66435 |
| O | -1.59691 | -7.52963 | -2.35140 |
| H | -4.35655 | -6.02303 | -1.77823 |
| C | -1.44428 | -7.94570 | 0.41013 |
| O | -2.58741 | -7.37830 | -0.30993 |
| H | -0.68540 | -8.21199 | -0.32955 |
| C | -0.91304 | -6.85664 | 1.33352 |
| H | -1.33356 | -9.31584 | 2.05688 |
| C | -4.13932 | -10.29298 | -0.99793 |
| H | -4.65353 | -11.05383 | -0.39311 |
| H | -4.34383 | -9.33111 | -0.51388 |
| H | -0.63009 | -5.96706 | 0.76031 |
| H | -0.02592 | -7.21542 | 1.86744 |
| H | -1.66640 | -6.56578 | 2.07499 |
| C | -4.76587 | -10.29348 | -2.40609 |
| H | -5.85785 | -10.22299 | -2.30851 |
| H | -4.56214 | -11.25656 | -2.89473 |
| H | -5.68843 | -7.47440 | -3.14275 |
| H | -3.19162 | -9.22680 | -3.47804 |
| H | -4.71405 | -9.34744 | -4.34800 |

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Compound **5.20**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -0.229477 kJ.

| | | | |
|---|---|---|---|
| C | 6.32720 | 0.06320 | -0.84910 |
| C | 5.25710 | 0.47030 | -1.88110 |
| C | 3.98920 | 1.02000 | -1.19430 |
| H | 4.93990 | -0.44580 | -2.37770 |
| C | 5.86700 | 1.41850 | -2.94720 |
| H | 5.92050 | -0.62170 | -0.10370 |
| H | 6.71890 | 0.93270 | -0.31960 |
| H | 7.16520 | -0.44160 | -1.32930 |
| H | 6.80830 | 1.00450 | -3.30990 |
| H | 6.12540 | 2.36740 | -2.47470 |
| O | 3.93450 | 1.19210 | 0.02410 |
| O | 2.97030 | 1.23860 | -2.04730 |
| C | 1.67140 | 1.57670 | -1.57200 |
| H | 1.48000 | 0.97810 | -0.67960 |
| C | 0.62940 | 1.13940 | -2.62850 |
| C | 1.57350 | 3.06320 | -1.17800 |
| H | 0.56110 | 3.32090 | -0.86760 |
| H | 1.85180 | 3.72140 | -2.00040 |
| H | 2.23580 | 3.29230 | -0.34290 |
| H | 0.86690 | 0.12940 | -2.96490 |
| C | 0.45350 | 2.06920 | -3.85030 |
| H | -0.33660 | 1.06200 | -2.12900 |
| C | -0.60310 | 1.53820 | -4.82960 |
| O | 1.68310 | 2.19610 | -4.55310 |
| H | 0.11470 | 3.03920 | -3.48380 |
| H | -1.57170 | 1.42770 | -4.34220 |
| H | -0.31630 | 0.56720 | -5.23420 |
| H | -0.73350 | 2.22300 | -5.66820 |
| C | 2.13040 | 3.41150 | -4.93400 |
| O | 1.51250 | 4.46960 | -4.82440 |
| C | 3.54660 | 3.38580 | -5.51320 |
| C | 4.50390 | 2.90260 | -4.42360 |
| H | 3.82840 | 4.42110 | -5.70730 |
| C | 3.60040 | 2.65270 | -6.86660 |
| H | 3.13160 | 1.66990 | -6.83050 |
| H | 4.62720 | 2.53680 | -7.21300 |
| H | 3.06710 | 3.22550 | -7.62580 |
| C | 4.98410 | 1.66640 | -4.16430 |
| H | 4.76740 | 3.68860 | -3.73040 |

| | | | |
|---|---|---|---|
| C | 4.68860 | 0.43060 | -4.99760 |
| H | 5.14330 | -0.46290 | -4.57130 |
| H | 5.09110 | 0.53680 | -6.00400 |
| H | 3.61400 | 0.25740 | -5.05530 |

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Compound **5.20**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -17.385281 kJ.

| | | | |
|---|---|---|---|
| C | 6.04140 | -0.57950 | -1.33610 |
| C | 5.12150 | 0.32460 | -2.17860 |
| C | 3.91760 | 0.82000 | -1.35430 |
| H | 4.71260 | -0.29800 | -2.97310 |
| C | 5.93310 | 1.48420 | -2.81440 |
| H | 5.48020 | -1.39010 | -0.86930 |
| H | 6.53160 | -0.01730 | -0.54000 |
| H | 6.81840 | -1.03230 | -1.95170 |
| H | 6.81350 | 1.08890 | -3.32180 |
| H | 6.31480 | 2.11580 | -2.01040 |
| O | 3.92950 | 0.82770 | -0.12290 |
| O | 2.88940 | 1.22410 | -2.12230 |
| C | 1.67630 | 1.69170 | -1.54430 |
| H | 1.50400 | 1.14610 | -0.61480 |
| C | 0.49640 | 1.34470 | -2.48250 |
| C | 1.78290 | 3.18950 | -1.20630 |
| H | 0.84390 | 3.57110 | -0.80570 |
| H | 2.04450 | 3.78400 | -2.08190 |
| H | 2.55350 | 3.36390 | -0.45500 |
| H | 0.54310 | 0.28470 | -2.73450 |
| C | 0.37640 | 2.18120 | -3.77670 |
| H | -0.42550 | 1.47090 | -1.91440 |
| C | -0.86660 | 1.80290 | -4.59430 |
| O | 1.51830 | 1.96790 | -4.59610 |
| H | 0.28430 | 3.23100 | -3.49520 |
| H | -1.77870 | 1.95280 | -4.01640 |
| H | -0.83350 | 0.75900 | -4.90720 |
| H | -0.94170 | 2.41770 | -5.49180 |
| C | 2.21960 | 3.01430 | -5.08230 |
| O | 1.89850 | 4.19860 | -4.99420 |
| C | 3.52570 | 2.59710 | -5.76430 |
| C | 4.37190 | 1.83390 | -4.75700 |
| H | 4.05080 | 3.50720 | -6.05090 |
| C | 3.26840 | 1.77430 | -7.03740 |
| H | 2.74700 | 0.84200 | -6.81630 |
| H | 4.20500 | 1.52400 | -7.53560 |
| H | 2.65820 | 2.33470 | -7.74670 |
| C | 5.18430 | 2.35860 | -3.81540 |
| H | 4.23970 | 0.76330 | -4.78980 |
| C | 5.43530 | 3.84870 | -3.65100 |
| H | 6.49470 | 4.06810 | -3.78500 |
| H | 5.14700 | 4.16420 | -2.64780 |
| H | 4.87560 | 4.46320 | -4.35360 |

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Compound **5.20**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in tetrahydrofuran was used.

Electronic Energy: -886.611209454 hartree.
Free Energy: -886.278812 hartree.

| | | | |
|---|---|---|---|
| C | 4.81593 | 3.04108 | -1.16912 |
| C | 5.10542 | 1.58958 | -1.53569 |
| C | 3.85252 | 0.75059 | -1.74115 |
| H | 5.64273 | 1.10580 | -0.71038 |
| C | 5.98895 | 1.43228 | -2.80033 |
| H | 4.25882 | 3.10389 | -0.23024 |
| H | 4.21977 | 3.53454 | -1.94262 |
| H | 5.75421 | 3.59195 | -1.04727 |
| H | 6.13976 | 0.36176 | -2.97090 |
| H | 6.96772 | 1.87787 | -2.59013 |
| O | 3.88781 | -0.44072 | -1.96307 |
| O | 2.71607 | 1.45601 | -1.68009 |
| C | 1.49646 | 0.74240 | -1.99231 |
| H | 1.70918 | 0.11187 | -2.86019 |
| C | 0.43912 | 1.78024 | -2.34992 |
| C | 1.06983 | -0.11002 | -0.80962 |
| H | 0.11089 | -0.59166 | -1.02556 |
| H | 0.94809 | 0.51585 | 0.08064 |
| H | 1.80842 | -0.88657 | -0.60164 |
| H | -0.41650 | 1.23975 | -2.77346 |
| C | 0.89786 | 2.86361 | -3.31825 |
| H | 0.08555 | 2.28043 | -1.43974 |
| C | -0.26397 | 3.65917 | -3.88526 |
| O | 1.62027 | 2.20271 | -4.38026 |
| H | 1.60443 | 3.53099 | -2.81663 |
| H | -0.83767 | 4.11398 | -3.07139 |

| | | | |
|---|---|---|---|
| H | -0.93124 | 3.00259 | -4.45333 |
| H | 0.09726 | 4.45347 | -4.54227 |
| C | 2.56008 | 2.92833 | -5.00705 |
| O | 2.67421 | 4.12739 | -4.88635 |
| C | 3.52395 | 2.04383 | -5.77717 |
| C | 4.40325 | 1.44633 | -4.69389 |
| H | 4.09646 | 2.70761 | -6.43044 |
| C | 2.82549 | 0.96637 | -6.60343 |
| H | 2.25343 | 0.29400 | -5.95814 |
| H | 3.56830 | 0.37254 | -7.14427 |
| H | 2.14112 | 1.40780 | -7.33407 |
| C | 5.36728 | 2.08599 | -4.01893 |
| H | 4.12834 | 0.43716 | -4.38456 |
| C | 5.86304 | 3.46717 | -4.35432 |
| H | 6.92762 | 3.42023 | -4.61795 |
| H | 5.78608 | 4.13320 | -3.48760 |
| H | 5.31807 | 3.93140 | -5.17754 |

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Compound **5.20**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in tetrahydrofuran was used.

Electronic Energy: -886.984291069 hartree.
Free Energy: -886.658039 hartree.

| | | | |
|---|---|---|---|
| C | 5.62966 | 0.91653 | -0.40247 |
| C | 5.16007 | 0.76153 | -1.86151 |
| C | 3.63482 | 0.67211 | -1.89283 |
| H | 5.49726 | -0.21285 | -2.22803 |
| C | 5.76322 | 1.87401 | -2.75628 |
| H | 5.24657 | 0.10494 | 0.22694 |
| H | 5.29378 | 1.86880 | 0.02204 |
| H | 6.72427 | 0.88945 | -0.35590 |
| H | 6.85294 | 1.72473 | -2.74913 |
| H | 5.56609 | 2.84732 | -2.29478 |
| O | 3.03827 | -0.37736 | -2.05661 |
| O | 3.03386 | 1.85222 | -1.64037 |
| C | 1.59845 | 1.85796 | -1.34521 |
| H | 1.25679 | 0.82280 | -1.37444 |
| C | 0.83281 | 2.71094 | -2.36315 |
| C | 1.45907 | 2.41061 | 0.07038 |
| H | 0.40918 | 2.39124 | 0.38323 |
| H | 1.81689 | 3.44512 | 0.12788 |
| H | 2.03553 | 1.80514 | 0.77806 |
| H | -0.15811 | 2.89779 | -1.92870 |
| C | 0.57961 | 2.14671 | -3.77174 |
| H | 1.31597 | 3.69105 | -2.45289 |
| C | 0.04027 | 0.72458 | -3.81661 |
| O | 1.81239 | 2.14084 | -4.54863 |
| H | -0.11496 | 2.82604 | -4.27283 |
| H | -0.87409 | 0.64898 | -3.21697 |
| H | 0.77235 | 0.00911 | -3.43077 |
| H | -0.20546 | 0.44504 | -4.84666 |
| C | 2.17570 | 3.27888 | -5.17052 |
| O | 1.48931 | 4.28151 | -5.22264 |
| C | 3.58441 | 3.15079 | -5.76933 |
| C | 4.49077 | 2.90087 | -4.57843 |
| H | 3.80325 | 4.15102 | -6.16258 |
| C | 3.57452 | 2.16725 | -6.94999 |
| H | 3.29826 | 1.15585 | -6.64198 |
| H | 4.55380 | 2.13302 | -7.43734 |
| H | 2.84694 | 2.50340 | -7.69845 |
| C | 5.23068 | 1.85471 | -4.17769 |
| H | 4.40314 | 3.71489 | -3.85653 |
| C | 5.54171 | 0.59426 | -4.95317 |
| H | 5.44860 | 0.71619 | -6.03152 |
| H | 4.88376 | -0.23300 | -4.65399 |
| H | 6.56943 | 0.26847 | -4.74429 |

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Compound **5.20**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -886.966088041 hartree.
Free Energy: -886.639668 hartree.

| | | | |
|---|---|---|---|
| C | 5.94109 | 0.86502 | -0.44193 |
| C | 5.29683 | 0.70471 | -1.83523 |
| C | 3.78160 | 0.62994 | -1.65018 |
| H | 5.57209 | -0.28414 | -2.21703 |
| C | 5.81299 | 1.79350 | -2.80591 |
| H | 5.62389 | 0.06092 | 0.22955 |
| H | 5.66259 | 1.82413 | 0.00945 |
| H | 7.03316 | 0.83325 | -0.52463 |
| H | 6.89870 | 1.63530 | -2.89942 |
| H | 5.67281 | 2.77641 | -2.34422 |
| O | 3.20068 | -0.41103 | -1.41274 |
| O | 3.17331 | 1.83409 | -1.68863 |
| C | 1.76568 | 1.87942 | -1.30412 |

| | | | |
|---|---|---|---|
| H | 1.66288 | 1.21945 | -0.43658 |
| C | 0.81246 | 1.33047 | -2.38350 |
| C | 1.50385 | 3.32358 | -0.89535 |
| H | 0.46172 | 3.44546 | -0.57967 |
| H | 1.69691 | 4.01491 | -1.72145 |
| H | 2.15116 | 3.60498 | -0.05916 |
| H | 1.14968 | 0.33017 | -2.67093 |
| C | 0.56543 | 2.17098 | -3.63699 |
| H | -0.15961 | 1.19828 | -1.88833 |
| C | -0.55731 | 1.60955 | -4.50625 |
| O | 1.79747 | 2.16721 | -4.40661 |
| H | 0.33911 | 3.21012 | -3.38542 |
| H | -1.50468 | 1.60754 | -3.95560 |
| H | -0.33408 | 0.58197 | -4.81400 |
| H | -0.68469 | 2.22567 | -5.40128 |
| C | 2.13668 | 3.29549 | -5.06659 |
| O | 1.44579 | 4.29115 | -5.12036 |
| C | 3.52650 | 3.14961 | -5.70599 |
| C | 4.47864 | 2.85700 | -4.56333 |
| H | 3.75139 | 4.15338 | -6.08595 |
| C | 3.45035 | 2.19559 | -6.90966 |
| H | 3.11812 | 1.19646 | -6.61820 |
| H | 4.42296 | 2.11604 | -7.40503 |
| H | 2.73636 | 2.58900 | -7.64201 |
| C | 5.16220 | 1.76955 | -4.17704 |
| H | 4.49088 | 3.68923 | -3.85774 |
| C | 5.32592 | 0.46699 | -4.92790 |
| H | 6.34868 | 0.08644 | -4.80508 |
| H | 5.13363 | 0.55524 | -5.99559 |
| H | 4.65421 | -0.30752 | -4.53297 |

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Compound **5.20**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in tetrahydrofuran was used.

Electronic Energy: -886.990807730 hartree.
Free Energy: -886.664490 hartree.

| | | | |
|---|---|---|---|
| C | 3.01970 | -1.29845 | 1.20270 |
| C | 2.70125 | -1.03784 | -0.27344 |
| C | 1.32079 | -1.52275 | -0.71257 |
| H | 3.39920 | -1.62409 | -0.88379 |
| C | 2.90007 | 0.44305 | -0.73035 |
| H | 2.98570 | -2.37145 | 1.42363 |
| H | 2.31654 | -0.80143 | 1.87455 |
| H | 4.02981 | -0.94177 | 1.43558 |
| H | 2.78587 | 0.45911 | -1.81992 |
| H | 3.94130 | 0.71169 | -0.51095 |
| O | 1.05614 | -1.81175 | -1.86597 |
| O | 0.43284 | -1.57885 | 0.29776 |
| C | -0.91121 | -2.08177 | 0.00122 |
| H | -1.13292 | -1.80454 | -1.03076 |
| C | -1.87067 | -1.39955 | 0.99189 |
| C | -0.89323 | -3.60041 | 0.13328 |
| H | -1.87947 | -4.00842 | -0.11582 |
| H | -0.64522 | -3.90165 | 1.15774 |
| H | -0.16063 | -4.04173 | -0.54998 |
| H | -2.57843 | -2.13992 | 1.38438 |
| C | -2.70462 | -0.23944 | 0.43063 |
| H | -1.28880 | -1.04199 | 1.84728 |
| C | -3.72574 | -0.64633 | -0.62246 |
| O | -1.83853 | 0.74817 | -0.20280 |
| H | -3.21080 | 0.25371 | 1.26478 |
| H | -4.44704 | -1.34829 | -0.18942 |
| H | -3.25471 | -1.12778 | -1.48649 |
| H | -4.27534 | 0.23085 | -0.97981 |
| C | -1.26427 | 1.68562 | 0.57965 |
| O | -1.44720 | 1.77760 | 1.77811 |
| C | -0.33763 | 2.59255 | -0.23134 |
| C | 0.80480 | 1.74081 | -0.74444 |
| H | 0.02434 | 3.33795 | 0.48193 |
| C | -1.08578 | 3.30546 | -1.37108 |
| H | -1.45382 | 2.58902 | -2.11241 |
| H | -0.41286 | 4.00642 | -1.87724 |
| H | -1.94206 | 3.87305 | -0.98876 |
| C | 1.95353 | 1.45564 | -0.10835 |
| H | 0.60778 | 1.25011 | -1.69748 |
| C | 2.35359 | 2.05715 | 1.21941 |
| H | 2.09531 | 1.40249 | 2.06164 |
| H | 1.86848 | 3.02064 | 1.40439 |
| H | 3.43827 | 2.21422 | 1.26152 |

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Compound **5.20**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -886.972976297 hartree.
Free Energy: -886.646297 hartree.

| | | | |
|---|---|---|---|
| C | 5.61144 | 2.36732 | -0.87052 |
| C | 5.34024 | 1.04502 | -1.59735 |
| C | 3.86363 | 0.66567 | -1.69234 |
| H | 5.79582 | 0.22859 | -1.02282 |
| C | 5.96529 | 0.95426 | -3.02641 |
| H | 5.21791 | 2.33910 | 0.15110 |
| H | 5.14868 | 3.21666 | -1.37758 |
| H | 6.69101 | 2.54671 | -0.80937 |
| H | 5.82661 | -0.07568 | -3.37134 |
| H | 7.04596 | 1.12157 | -2.92606 |
| O | 3.48118 | -0.47145 | -1.88517 |
| O | 3.03970 | 1.72821 | -1.57553 |
| C | 1.60271 | 1.47852 | -1.66508 |
| H | 1.47340 | 0.62959 | -2.33953 |
| C | 0.97002 | 2.76005 | -2.23945 |
| C | 1.08696 | 1.11196 | -0.27690 |
| H | 0.01078 | 0.90795 | -0.31717 |
| H | 1.25504 | 1.93302 | 0.42932 |
| H | 1.59076 | 0.21518 | 0.09493 |
| H | 0.10734 | 3.05616 | -1.62882 |
| C | 0.48674 | 2.66363 | -3.69447 |
| H | 1.69982 | 3.57135 | -2.16418 |
| C | -0.69446 | 1.72439 | -3.90485 |
| O | 1.55059 | 2.16645 | -4.55223 |
| H | 0.23165 | 3.67096 | -4.03675 |
| H | -1.55646 | 2.06887 | -3.32306 |
| H | -0.45647 | 0.70076 | -3.59642 |
| H | -0.97919 | 1.70068 | -4.96127 |
| C | 2.48405 | 3.05368 | -4.97058 |
| O | 2.46688 | 4.23510 | -4.69322 |
| C | 3.57702 | 2.36267 | -5.78641 |
| C | 4.37220 | 1.49629 | -4.82998 |
| H | 4.20004 | 3.17798 | -6.16707 |
| C | 3.00925 | 1.55555 | -6.96582 |
| H | 2.36665 | 0.74461 | -6.61030 |
| H | 3.82806 | 1.11694 | -7.54605 |
| H | 2.41947 | 2.19132 | -7.63537 |
| C | 5.37443 | 1.91483 | -4.04071 |
| H | 4.02078 | 0.46950 | -4.73308 |
| C | 5.91180 | 3.33256 | -4.08399 |
| H | 5.18999 | 4.05556 | -3.68540 |
| H | 6.13179 | 3.64595 | -5.11185 |
| H | 6.83578 | 3.42695 | -3.50588 |

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Compound **5.20**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in tetrahydrofuran was used.

Electronic Energy: -886.603934564 hartree.
Free Energy: -886.273252 hartree.

| | | | |
|---|---|---|---|
| C | 6.28587 | 0.10462 | -0.82498 |
| C | 5.24081 | 0.42857 | -1.88587 |
| C | 3.97606 | 0.95651 | -1.23374 |
| H | 4.95600 | -0.48849 | -2.41652 |
| C | 5.80340 | 1.43440 | -2.91983 |
| H | 5.90273 | -0.61131 | -0.09300 |
| H | 6.58197 | 1.00935 | -0.28516 |
| H | 7.17603 | -0.32414 | -1.29483 |
| H | 6.76242 | 1.01794 | -3.25945 |
| H | 6.02505 | 2.37934 | -2.40907 |
| O | 3.87352 | 1.24890 | -0.06244 |
| O | 2.97021 | 1.04812 | -2.11295 |
| C | 1.69778 | 1.52373 | -1.61758 |
| H | 1.50166 | 0.99011 | -0.68181 |
| C | 0.64233 | 1.11794 | -2.64677 |
| C | 1.75637 | 3.01848 | -1.33932 |
| H | 0.76703 | 3.38092 | -1.04067 |
| H | 2.07436 | 3.57439 | -2.22672 |
| H | 2.45826 | 3.22480 | -0.52937 |
| H | 0.86237 | 0.10032 | -2.99070 |
| C | 0.49006 | 2.05249 | -3.83973 |
| H | -0.32969 | 1.08442 | -2.14053 |
| C | -0.48599 | 1.52923 | -4.87771 |
| O | 1.78594 | 2.19692 | -4.45633 |
| H | 0.17128 | 3.04126 | -3.50079 |
| H | -1.47985 | 1.40451 | -4.43688 |
| H | -0.15217 | 0.56076 | -5.26416 |
| H | -0.56557 | 2.23244 | -5.71229 |
| C | 2.13692 | 3.41763 | -4.88755 |
| O | 1.41567 | 4.38823 | -4.83566 |
| C | 3.54966 | 3.41910 | -5.45746 |
| C | 4.51230 | 2.91833 | -4.39993 |
| H | 3.77345 | 4.47477 | -5.63429 |
| C | 3.52693 | 2.71613 | -6.82343 |
| H | 3.04615 | 1.73759 | -6.77471 |
| H | 4.54352 | 2.59097 | -7.20727 |
| H | 2.96631 | 3.32940 | -7.53600 |
| C | 4.91937 | 1.67481 | -4.12195 |
| H | 4.84235 | 3.70508 | -3.72074 |
| C | 4.53578 | 0.42951 | -4.88304 |
| H | 5.22147 | -0.39221 | -4.65107 |

| | | | |
|---|---|---|---|
| H | 4.55735 | 0.57336 | -5.96335 |
| H | 3.52463 | 0.11535 | -4.59973 |

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Compound **5.21**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +19.061619 kJ.

| | | | |
|---|---|---|---|
| H | -10.78210 | -3.05770 | 13.25120 |
| C | -9.90650 | -3.70620 | 13.24190 |
| O | -10.94540 | -5.40500 | 11.90240 |
| C | -9.56750 | -3.87110 | 10.68380 |
| C | -10.01070 | -5.33890 | 10.82540 |
| C | -9.05490 | -3.35200 | 12.02560 |
| C | -10.32710 | -5.18350 | 13.16620 |
| H | -8.78350 | -3.77330 | 9.93280 |
| C | -10.67050 | -5.89660 | 9.54550 |
| C | -11.28280 | -5.57870 | 14.28160 |
| H | -9.34140 | -3.51040 | 14.15320 |
| H | -10.40370 | -3.24760 | 10.36810 |
| H | -9.13210 | -5.94790 | 11.05020 |
| H | -9.43600 | -5.80560 | 13.25270 |
| O | -8.03960 | -2.66520 | 12.11530 |
| C | -11.08510 | -7.36600 | 9.67420 |
| H | -9.98530 | -5.81260 | 8.70250 |
| H | -11.55520 | -5.31080 | 9.29610 |
| O | -12.19670 | -7.74980 | 9.31310 |
| O | -10.12750 | -8.13940 | 10.22780 |
| C | -11.42440 | -6.81170 | 14.81570 |
| C | -12.43780 | -7.08690 | 15.91010 |
| C | -10.64390 | -8.03420 | 14.34240 |
| H | -11.93960 | -7.46880 | 16.80140 |
| H | -13.15800 | -7.83470 | 15.57660 |
| H | -12.98830 | -6.18800 | 16.18890 |
| C | -11.19820 | -8.60100 | 13.01930 |
| H | -10.63790 | -8.80500 | 15.11400 |
| H | -9.60090 | -7.74630 | 14.22170 |
| O | -12.32520 | -9.42010 | 13.30550 |
| C | -10.17000 | -9.44110 | 12.23330 |
| H | -11.48880 | -7.75400 | 12.40240 |
| H | -9.16350 | -9.05790 | 12.40270 |
| C | -10.42580 | -9.44810 | 10.71070 |
| H | -10.17170 | -10.45870 | 12.62520 |
| C | -13.52960 | -8.96640 | 12.70490 |
| H | -14.34820 | -9.63370 | 12.97360 |
| H | -13.44980 | -8.95330 | 11.61730 |
| H | -13.78690 | -7.96310 | 13.04730 |
| C | -9.52890 | -10.45930 | 9.97360 |
| H | -11.46790 | -9.71890 | 10.53500 |
| H | -8.48060 | -10.19000 | 10.10870 |
| C | -9.85160 | -10.57180 | 8.47460 |
| H | -9.65470 | -11.44090 | 10.43230 |
| H | -10.90690 | -10.81750 | 8.34640 |
| C | -8.99400 | -11.62530 | 7.76290 |
| H | -9.70390 | -9.60540 | 7.99130 |
| H | -9.14810 | -12.61640 | 8.19060 |
| H | -7.93230 | -11.38810 | 7.83850 |
| H | -9.24620 | -11.67980 | 6.70340 |
| H | -11.91110 | -4.78120 | 14.65120 |

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Compound **5.20**
This structure was assigned as ambiguous.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +25.884905 kJ.

| | | | |
|---|---|---|---|
| H | -12.02850 | -4.47340 | 12.56890 |
| C | -11.09640 | -3.96740 | 12.81980 |
| O | -9.68770 | -5.88300 | 12.37220 |
| C | -9.95940 | -4.29260 | 10.54550 |
| C | -9.01940 | -5.28380 | 11.26200 |
| C | -10.54330 | -3.32180 | 11.55900 |
| C | -10.07990 | -4.97150 | 13.39140 |
| H | -9.42630 | -3.73990 | 9.77180 |
| C | -8.49010 | -6.41080 | 10.35020 |
| C | -10.66940 | -5.66860 | 14.61250 |
| H | -11.33050 | -3.19300 | 13.55020 |
| H | -10.78700 | -4.81180 | 10.06320 |
| H | -8.15180 | -4.73750 | 11.63660 |
| H | -9.19440 | -4.43660 | 13.74010 |
| O | -10.59160 | -2.10950 | 11.36170 |
| C | -9.58600 | -7.36590 | 9.88300 |
| H | -7.73590 | -6.98940 | 10.88360 |
| H | -7.99900 | -5.98800 | 9.47410 |
| O | -10.30050 | -7.10360 | 8.91530 |
| O | -9.68190 | -8.45670 | 10.66710 |
| C | -10.89490 | -6.98020 | 14.85770 |
| C | -11.52570 | -7.40570 | 16.17350 |
| C | -10.55440 | -8.14730 | 13.93110 |
| H | -10.84520 | -8.05150 | 16.72890 |

| | | | |
|---|---|---|---|
| H | -12.44740 | -7.95930 | 15.9940 |
| H | -11.76930 | -6.55280 | 16.80730 |
| C | -11.64960 | -8.46950 | 12.88970 |
| H | -10.37310 | -9.02820 | 14.54770 |
| H | -9.60220 | -7.96660 | 13.43620 |
| O | -12.83500 | -8.80240 | 13.60390 |
| C | -11.26290 | -9.67830 | 12.00110 |
| H | -11.81890 | -7.58200 | 12.27620 |
| H | -10.49670 | -10.27370 | 12.49850 |
| C | -10.80500 | -9.32330 | 10.57170 |
| H | -12.12080 | -10.34510 | 11.91470 |
| C | -14.03160 | -8.48340 | 12.90990 |
| H | -14.89110 | -8.79910 | 13.50100 |
| H | -14.08490 | -8.98580 | 11.94350 |
| H | -14.11460 | -7.40780 | 12.74870 |
| C | -10.43120 | -10.59440 | 9.77850 |
| H | -11.63670 | -8.82240 | 10.07300 |
| H | -9.56790 | -11.07440 | 10.24130 |
| C | -10.15080 | -10.34960 | 8.28660 |
| H | -11.25250 | -11.30770 | 9.85830 |
| H | -10.99210 | -9.81920 | 7.83810 |
| C | -9.89710 | -11.64890 | 7.51230 |
| H | -9.28420 | -9.69760 | 8.17470 |
| H | -10.76000 | -12.31390 | 7.55950 |
| H | -9.03650 | -12.18600 | 7.91220 |
| H | -9.69760 | -11.44080 | 6.46060 |
| H | -10.95820 | -4.97220 | 15.38640 |

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Compound **5.20**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in ethanol was used.

Electronic Energy: -1078.45504411 hartree.
Free Energy: -1078.059503 hartree.

| | | | |
|---|---|---|---|
| H | -4.15560 | -0.90349 | 0.72505 |
| C | -3.68754 | -1.01107 | -0.26344 |
| O | -1.48953 | -0.60585 | 0.64455 |
| C | -2.09961 | -2.92146 | 0.34504 |
| C | -0.98290 | -1.87560 | 0.25313 |
| C | -3.31133 | -2.46531 | -0.43869 |
| C | -2.44606 | -0.10794 | -0.30332 |
| H | -1.77213 | -3.89824 | -0.02024 |
| C | 0.19562 | -2.20115 | 1.15937 |
| C | -2.77800 | 1.32379 | 0.01523 |
| H | -4.41408 | -0.72562 | -1.02878 |
| H | -2.39955 | -3.01531 | 1.39805 |
| H | -0.62901 | -1.81130 | -0.78616 |
| H | -1.99085 | -0.17554 | -1.30258 |
| O | -3.94632 | -3.22029 | -1.15132 |
| C | 1.26350 | -1.12917 | 1.12034 |
| H | 0.64333 | -3.14910 | 0.83910 |
| H | -0.13157 | -2.30477 | 2.19716 |
| O | 1.78457 | -0.65537 | 2.10807 |
| O | 1.56819 | -0.77406 | -0.13163 |
| C | -2.09290 | 2.38573 | -0.43467 |
| C | -2.47752 | 3.78852 | -0.05752 |
| C | -0.84291 | 2.24645 | -1.27856 |
| H | -2.75194 | 4.36339 | -0.95092 |
| H | -1.62267 | 4.30625 | 0.39623 |
| H | -3.31691 | 3.81137 | 0.64324 |
| C | 0.34741 | 1.80895 | -0.41637 |
| H | -0.60221 | 3.19558 | -1.77233 |
| H | -0.98897 | 1.49700 | -2.06426 |
| O | 0.75921 | 2.87015 | 0.44595 |
| C | 1.56047 | 1.33642 | -1.21351 |
| H | 0.00118 | 0.97488 | 0.20022 |
| H | 1.24534 | 0.80410 | -2.11889 |
| C | 2.40679 | 0.39325 | -0.36617 |
| H | 2.16080 | 2.20044 | -1.52040 |
| C | 0.37518 | 2.69218 | 1.79777 |
| H | 0.74403 | 3.55877 | 2.35298 |
| H | 0.81757 | 1.77960 | 2.21944 |
| H | -0.71503 | 2.63428 | 1.91205 |
| C | 3.69026 | -0.07331 | -1.02960 |
| H | 2.62385 | 0.85299 | 0.60306 |
| H | 3.43978 | -0.56917 | -1.97754 |
| C | 4.51499 | -1.00998 | -0.14929 |
| H | 4.28030 | 0.81765 | -1.27942 |
| H | 4.74274 | -0.50558 | 0.79865 |
| C | 5.80963 | -1.44405 | -0.82910 |
| H | 3.91521 | -1.89369 | 0.10234 |
| H | 6.43232 | -0.57671 | -1.07608 |
| H | 5.60264 | -1.98111 | -1.76170 |
| H | 6.39811 | -2.10534 | -0.18530 |
| H | -3.63617 | 1.48444 | 0.66832 |

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Compound **5.20**
This structure was assigned as correct.
B3LYP/6-31g(d)

SMD implicit solvation in ethanol was used.

Electronic Energy: -1078.91126686 hartree.
Free Energy: -1078.520716 hartree.

| | | | |
|---|---|---|---|
| H | -4.22878 | -0.87147 | 0.67627 |
| C | -3.73867 | -1.01817 | -0.29752 |
| O | -1.53381 | -0.58731 | 0.62521 |
| C | -2.16415 | -2.92175 | 0.39844 |
| C | -1.02932 | -1.88588 | 0.29469 |
| C | -3.37042 | -2.48443 | -0.41217 |
| C | -2.49071 | -0.11398 | -0.35276 |
| H | -1.84007 | -3.91252 | 0.06581 |
| C | 0.13484 | -2.18528 | 1.24081 |
| C | -2.81550 | 1.33245 | -0.08593 |
| H | -4.45386 | -0.75877 | -1.08408 |
| H | -2.47739 | -2.99231 | 1.45021 |
| H | -0.65373 | -1.86829 | -0.73791 |
| H | -2.02709 | -0.21813 | -1.34434 |
| O | -4.00942 | -3.26715 | -1.10293 |
| C | 1.21865 | -1.12110 | 1.20593 |
| H | 0.58033 | -3.14753 | 0.95939 |
| H | -0.21575 | -2.26247 | 2.27373 |
| O | 1.69442 | -0.60542 | 2.20372 |
| O | 1.58720 | -0.82551 | -0.05077 |
| C | -2.08483 | 2.38671 | -0.49661 |
| C | -2.52256 | 3.79826 | -0.20140 |
| C | -0.77880 | 2.23360 | -1.25713 |
| H | -2.73113 | 4.33888 | -1.13588 |
| H | -1.72701 | 4.35949 | 0.30550 |
| H | -3.42405 | 3.83212 | 0.41972 |
| C | 0.42107 | 1.86762 | -0.35109 |
| H | -0.54147 | 3.15592 | -1.80175 |
| H | -0.88103 | 1.43926 | -2.00594 |
| O | 0.87300 | 3.01039 | 0.39868 |
| C | 1.61792 | 1.30798 | -1.13928 |
| H | 0.07143 | 1.10802 | 0.35015 |
| H | 1.27363 | 0.78555 | -2.03969 |
| C | 2.46056 | 0.33085 | -0.31480 |
| H | 2.24996 | 2.14147 | -1.46880 |
| C | 0.52710 | 2.99057 | 1.77946 |
| H | 0.94270 | 3.90137 | 2.22274 |
| H | 0.95609 | 2.11867 | 2.29262 |
| H | -0.55958 | 2.98739 | 1.93772 |
| C | 3.70508 | -0.17720 | -1.03726 |
| H | 2.72934 | 0.76910 | 0.64898 |
| H | 3.39677 | -0.67756 | -1.96621 |
| C | 4.57814 | -1.11903 | -0.19865 |
| H | 4.29333 | 0.70150 | -1.33425 |
| H | 4.89979 | -0.59724 | 0.71325 |
| C | 5.80590 | -1.62291 | -0.96220 |
| H | 3.97735 | -1.97684 | 0.13100 |
| H | 6.44330 | -0.79109 | -1.28881 |
| H | 5.51482 | -2.18802 | -1.85702 |
| H | 6.41857 | -2.28376 | -0.33698 |
| H | -3.72346 | 1.51766 | 0.48819 |

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Compound **5.20**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1078.88333190 hartree.
Free Energy: -1078.492878 hartree.

| | | | |
|---|---|---|---|
| H | -4.23522 | -0.83596 | 0.69627 |
| C | -3.76098 | -0.99002 | -0.28397 |
| O | -1.54528 | -0.57347 | 0.61730 |
| C | -2.19654 | -2.90282 | 0.41207 |
| C | -1.05308 | -1.87505 | 0.30135 |
| C | -3.39914 | -2.46329 | -0.41663 |
| C | -2.50428 | -0.09788 | -0.35078 |
| H | -1.88763 | -3.90127 | 0.08795 |
| C | 0.11031 | -2.17003 | 1.25238 |
| C | -2.80746 | 1.35474 | -0.09208 |
| H | -4.48468 | -0.72762 | -1.06132 |
| H | -2.50727 | -2.95936 | 1.46535 |
| H | -0.66953 | -1.87117 | -0.73060 |
| H | -2.05163 | -0.21138 | -1.34927 |
| O | -4.01322 | -3.22942 | -1.13296 |
| C | 1.19285 | -1.09916 | 1.21756 |
| H | 0.55296 | -3.13601 | 0.97867 |
| H | -0.24274 | -2.23507 | 2.28490 |
| O | 1.62778 | -0.54194 | 2.20184 |
| O | 1.59560 | -0.85508 | -0.04969 |
| C | -2.06347 | 2.39527 | -0.50868 |
| C | -2.46439 | 3.81593 | -0.20356 |
| C | -0.76338 | 2.21902 | -1.27204 |
| H | -2.66585 | 4.36714 | -1.13276 |
| H | -1.64620 | 4.34643 | 0.29879 |
| H | -3.35892 | 3.86852 | 0.42511 |
| C | 0.42602 | 1.84424 | -0.35457 |

| | | | |
|---|---|---|---|
| H | -0.51007 | 3.13635 | -1.81718 |
| H | -0.87648 | 1.42427 | -2.01968 |
| O | 0.86489 | 2.98361 | 0.39290 |
| C | 1.62704 | 1.28292 | -1.13708 |
| H | 0.06186 | 1.08015 | 0.33446 |
| H | 1.28961 | 0.76265 | -2.04239 |
| C | 2.46164 | 0.29891 | -0.31113 |
| H | 2.25892 | 2.12052 | -1.45562 |
| C | 0.59106 | 2.92610 | 1.78715 |
| H | 1.03690 | 3.82268 | 2.22799 |
| H | 1.03383 | 2.03619 | 2.25307 |
| H | -0.48825 | 2.92773 | 1.99570 |
| C | 3.71190 | -0.20090 | -1.03245 |
| H | 2.72745 | 0.73552 | 0.65465 |
| H | 3.41237 | -0.67957 | -1.97570 |
| C | 4.57217 | -1.16673 | -0.20822 |
| H | 4.30906 | 0.68010 | -1.30640 |
| H | 4.84970 | -0.68650 | 0.73989 |
| C | 5.83587 | -1.61369 | -0.95004 |
| H | 3.97227 | -2.04601 | 0.05724 |
| H | 6.47547 | -0.75791 | -1.19914 |
| H | 5.58620 | -2.12367 | -1.88874 |
| H | 6.42910 | -2.30641 | -0.34276 |
| H | -3.70632 | 1.55481 | 0.49075 |

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Compound **5.20**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
SMD implicit solvation in ethanol was used.

Electronic Energy: -1078.91007250 hartree.
Free Energy: -1078.519437 hartree.

| | | | |
|---|---|---|---|
| H | -2.88403 | -0.27578 | 1.51857 |
| C | -3.40182 | -0.75285 | 0.67468 |
| O | -1.42643 | -0.66762 | -0.75166 |
| C | -1.82889 | -2.74989 | 0.46291 |
| C | -1.30051 | -2.08941 | -0.82654 |
| C | -3.21708 | -2.24953 | 0.79998 |
| C | -2.77460 | -0.21793 | -0.64074 |
| H | -1.84211 | -3.83968 | 0.36693 |
| C | 0.18244 | -2.38289 | -1.11621 |
| C | -2.88239 | 1.28258 | -0.70748 |
| H | -4.46570 | -0.50593 | 0.73381 |
| H | -1.16536 | -2.48205 | 1.29564 |
| H | -1.88996 | -2.45845 | -1.67853 |
| H | -3.35100 | -0.64344 | -1.48113 |
| O | -4.11813 | -2.99744 | 1.15642 |
| C | 1.08332 | -1.65782 | -0.13733 |
| H | 0.41622 | -2.06828 | -2.13603 |
| H | 0.35814 | -3.45920 | -1.02718 |
| O | 1.26297 | -2.01065 | 1.01818 |
| O | 1.62796 | -0.56209 | -0.68937 |
| C | -1.96860 | 2.25231 | -0.88687 |
| C | -2.42838 | 3.69373 | -0.91999 |
| C | -0.47340 | 2.06098 | -1.09522 |
| H | -2.21391 | 4.14743 | -1.89843 |
| H | -1.88764 | 4.29058 | -0.17546 |
| H | -3.50262 | 3.79145 | -0.72949 |
| C | 0.36318 | 1.97042 | 0.19379 |
| H | -0.08929 | 2.91158 | -1.67466 |
| H | -0.27290 | 1.15959 | -1.67549 |
| O | 0.15497 | 3.18811 | 0.92627 |
| C | 1.86987 | 1.76435 | -0.11171 |
| H | -0.01196 | 1.13491 | 0.80222 |
| H | 2.08274 | 2.04540 | -1.15122 |
| C | 2.40442 | 0.35705 | 0.15205 |
| H | 2.45047 | 2.44727 | 0.51888 |
| C | 0.43649 | 3.08000 | 2.31329 |
| H | 0.21884 | 4.05450 | 2.76088 |
| H | 1.49019 | 2.83382 | 2.51144 |
| H | -0.19541 | 2.31704 | 2.79296 |
| C | 3.88705 | 0.20914 | -0.18937 |
| H | 2.22427 | 0.07314 | 1.19184 |
| H | 4.03163 | 0.45560 | -1.25064 |
| C | 4.48680 | -1.17110 | 0.11076 |
| H | 4.42769 | 0.97335 | 0.38574 |
| H | 4.30523 | -1.42786 | 1.16324 |
| C | 5.98924 | -1.23195 | -0.17782 |
| H | 3.97227 | -1.93393 | -0.48809 |
| H | 6.54347 | -0.51169 | 0.43755 |
| H | 6.20397 | -1.00377 | -1.22978 |
| H | 6.39274 | -2.22942 | 0.03415 |
| H | -3.91962 | 1.59817 | -0.58580 |

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Compound **5.20**

This structure was assigned as ambiguous.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1078.88333141 hartree.
Free Energy: -1078.492025 hartree.

| | | | |
|---|---|---|---|
| H | -2.85966 | -0.24407 | 1.52750 |
| C | -3.40572 | -0.70823 | 0.69495 |
| O | -1.44819 | -0.66147 | -0.75014 |
| C | -1.88022 | -2.74239 | 0.46213 |
| C | -1.33911 | -2.08022 | -0.82183 |
| C | -3.26771 | -2.21897 | 0.79711 |
| C | -2.78319 | -0.18544 | -0.62749 |
| H | -1.92327 | -3.83081 | 0.35703 |
| C | 0.14582 | -2.37851 | -1.09796 |
| C | -2.85499 | 1.31658 | -0.70337 |
| H | -4.46182 | -0.43585 | 0.77646 |
| H | -1.19783 | -2.50144 | 1.28725 |
| H | -1.92706 | -2.44306 | -1.68126 |
| H | -3.37715 | -0.60187 | -1.46341 |
| O | -4.19090 | -2.94681 | 1.10776 |
| C | 1.03012 | -1.64519 | -0.10430 |
| H | 0.39531 | -2.06580 | -2.11438 |
| H | 0.32209 | -3.45436 | -0.99986 |
| O | 1.13523 | -1.94700 | 1.06781 |
| O | 1.64824 | -0.59814 | -0.68787 |
| C | -1.91556 | 2.25761 | -0.89220 |
| C | -2.32811 | 3.71289 | -0.92406 |
| C | -0.42872 | 2.01769 | -1.10176 |
| H | -2.10239 | 4.15654 | -1.90425 |
| H | -1.75909 | 4.28158 | -0.18084 |
| H | -3.39772 | 3.84474 | -0.73105 |
| C | 0.40328 | 1.96475 | 0.19184 |
| H | -0.02607 | 2.83637 | -1.71389 |
| H | -0.25295 | 1.08573 | -1.63866 |
| O | 0.21360 | 3.20839 | 0.87422 |
| C | 1.90905 | 1.72833 | -0.10019 |
| H | 0.01382 | 1.15211 | 0.82388 |
| H | 2.13444 | 2.01394 | -1.13595 |
| C | 2.42106 | 0.30959 | 0.15595 |
| H | 2.49356 | 2.40273 | 0.53692 |
| C | 0.46148 | 3.15197 | 2.26310 |
| H | 0.24484 | 4.14462 | 2.66715 |
| H | 1.50908 | 2.90300 | 2.49656 |
| H | -0.18640 | 2.41287 | 2.76025 |
| C | 3.90574 | 0.14782 | -0.17683 |
| H | 2.23536 | 0.01772 | 1.19359 |
| H | 4.06104 | 0.40333 | -1.23447 |
| C | 4.48272 | -1.24435 | 0.11136 |
| H | 4.45693 | 0.89825 | 0.40760 |
| H | 4.28620 | -1.51252 | 1.15772 |
| C | 5.98611 | -1.32660 | -0.17225 |
| H | 3.95591 | -1.98854 | -0.49881 |
| H | 6.54821 | -0.62012 | 0.45098 |
| H | 6.20683 | -1.09049 | -1.22053 |
| H | 6.37367 | -2.33096 | 0.03154 |
| H | -3.88186 | 1.66273 | -0.57655 |

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Compound **5.20**
This structure was assigned as ambiguous.
M06-2X/6-31g(d)
SMD implicit solvation in ethanol was used.

Electronic Energy: -1078.45332308 hartree.
Free Energy: -1078.057219 hartree.

| | | | |
|---|---|---|---|
| H | -4.31099 | 0.29143 | 0.69033 |
| C | -3.92636 | 0.00952 | -0.29930 |
| O | -1.68734 | -0.20076 | 0.59115 |
| C | -2.97843 | -2.24913 | 0.39739 |
| C | -1.59072 | -1.59319 | 0.32802 |
| C | -3.99504 | -1.49289 | -0.42688 |
| C | -2.46788 | 0.47257 | -0.40219 |
| H | -2.94364 | -3.29256 | 0.07344 |
| C | -0.66061 | -2.19235 | 1.36729 |
| C | -2.31797 | 1.95581 | -0.21389 |
| H | -4.54816 | 0.47500 | -1.06877 |
| H | -3.32289 | -2.21457 | 1.44066 |
| H | -1.16935 | -1.73440 | -0.67822 |
| H | -2.08372 | 0.17641 | -1.39059 |
| O | -4.81261 | -2.05602 | -1.13096 |
| C | 0.70145 | -1.54631 | 1.46050 |
| H | -0.50313 | -3.25523 | 1.14597 |
| H | -1.10955 | -2.12885 | 2.36304 |
| O | 1.36518 | -1.55356 | 2.47687 |
| O | 1.10790 | -0.99921 | 0.31302 |
| C | -1.20905 | 2.64199 | -0.52044 |
| C | -1.12416 | 4.12372 | -0.27220 |
| C | 0.01094 | 1.96770 | -1.10235 |
| H | -0.77271 | 4.64721 | -1.16946 |
| H | -0.40105 | 4.34396 | 0.52043 |
| H | -2.09541 | 4.53491 | 0.01750 |
| C | 1.18674 | 1.85443 | -0.12864 |
| H | 0.36593 | 2.52270 | -1.98212 |
| H | -0.23265 | 0.95393 | -1.43172 |

| | | | |
|---|---|---|---|
| O | 1.73643 | 3.15497 | 0.03351 |
| C | 2.25185 | 0.85342 | -0.62791 |
| H | 0.79930 | 1.51379 | 0.84670 |
| H | 2.00116 | 0.50370 | -1.63577 |
| C | 2.40062 | -0.33261 | 0.30939 |
| H | 3.22188 | 1.35916 | -0.69757 |
| C | 2.53694 | 3.27176 | 1.19103 |
| H | 1.95762 | 3.04300 | 2.09664 |
| H | 2.88703 | 4.30556 | 1.24091 |
| H | 3.41173 | 2.60753 | 1.15771 |
| C | 3.48260 | -1.33763 | -0.06414 |
| H | 2.57882 | 0.03358 | 1.32524 |
| H | 4.45407 | -0.83611 | 0.03464 |
| C | 3.34727 | -1.93923 | -1.46235 |
| H | 3.46643 | -2.14132 | 0.68418 |
| H | 2.33406 | -2.34051 | -1.58982 |
| C | 4.37164 | -3.04513 | -1.69857 |
| H | 3.47554 | -1.15726 | -2.22030 |
| H | 4.24860 | -3.85474 | -0.97051 |
| H | 5.39303 | -2.66044 | -1.59869 |
| H | 4.27190 | -3.47542 | -2.70010 |
| H | -3.16911 | 2.48132 | 0.21891 |

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Compound **5.22**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +3.354037 kJ.

| | | | |
|---|---|---|---|
| H | -3.75650 | -5.78180 | -0.48280 |
| C | -4.59330 | -6.30540 | -0.01790 |
| H | -5.21700 | -6.65970 | -0.83940 |
| C | -5.38740 | -5.32540 | 0.86260 |
| H | -5.77710 | -4.51940 | 0.24030 |
| H | -6.26330 | -5.82180 | 1.27220 |
| C | -4.52310 | -4.68800 | 1.94220 |
| H | -3.76470 | -4.02060 | 1.55850 |
| C | -4.58540 | -4.87650 | 3.27750 |
| C | -5.57140 | -5.79950 | 3.97730 |
| H | -5.05880 | -6.69400 | 4.33200 |
| H | -6.39470 | -6.12130 | 3.34550 |
| H | -6.01020 | -5.29570 | 4.83850 |
| C | -3.62790 | -4.15470 | 4.21660 |
| H | -3.00110 | -3.46390 | 3.65030 |
| H | -4.21980 | -3.53280 | 4.88840 |
| C | -2.72460 | -5.08270 | 5.05390 |
| H | -2.16820 | -4.48860 | 5.77850 |
| H | -3.32590 | -5.78360 | 5.63180 |
| C | -1.70880 | -5.86700 | 4.22670 |
| O | -0.58870 | -5.41130 | 3.99950 |
| O | -2.16920 | -7.05790 | 3.81500 |
| C | -1.31740 | -7.94950 | 3.09820 |
| H | -0.52180 | -7.38510 | 2.60890 |
| C | -0.66620 | -8.89520 | 4.12690 |
| H | 0.12650 | -9.48400 | 3.66530 |
| H | -0.18950 | -8.30100 | 4.90830 |
| O | -1.64810 | -9.77620 | 4.66130 |
| C | -1.29260 | -10.33620 | 5.91610 |
| H | -1.95920 | -11.17620 | 6.11240 |
| H | -0.27960 | -10.74080 | 5.88080 |
| C | -1.44430 | -9.34680 | 7.06010 |
| C | -1.74500 | -7.51720 | 9.18830 |
| C | -0.54870 | -9.37380 | 8.14940 |
| C | -2.49780 | -8.40830 | 7.04680 |
| C | -2.64650 | -7.49270 | 8.10660 |
| C | -0.69740 | -8.45860 | 9.21030 |
| H | 0.25620 | -10.09400 | 8.17300 |
| H | -3.18800 | -8.38880 | 6.21470 |
| H | -3.45240 | -6.77350 | 8.08910 |
| H | -0.00780 | -8.47890 | 10.04180 |
| H | -1.85850 | -6.81550 | 10.00220 |
| C | -2.13130 | -8.65360 | 1.98700 |
| H | -2.90280 | -9.24410 | 2.47740 |
| C | -1.27330 | -9.60260 | 1.13440 |
| H | -1.86700 | -10.05180 | 0.33760 |
| H | -0.87000 | -10.42030 | 1.73180 |
| H | -0.43670 | -9.07840 | 0.67130 |
| C | -2.78200 | -7.61000 | 1.09120 |
| H | -2.10840 | -6.83730 | 0.74900 |
| C | -4.08530 | -7.50550 | 0.76490 |
| C | -5.15820 | -8.49330 | 1.19470 |
| H | -5.68600 | -8.12260 | 2.07260 |
| H | -4.75530 | -9.47750 | 1.42670 |
| H | -5.88570 | -8.63240 | 0.39500 |

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Compound **5.22**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +13.600031 kJ.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -4.84190 | -6.58900 | 1.03010 | C | -2.96620 | -8.01330 | 2.08140 |
| C | -5.30600 | -7.21300 | 1.79560 | H | -2.67950 | -7.18610 | 1.44670 |
| H | -6.11290 | -7.75030 | 1.29630 | C | -4.27840 | -8.20270 | 2.32380 |
| C | -5.86810 | -6.29870 | 2.90370 | C | -4.83750 | -9.30390 | 3.20940 |
| H | -6.41540 | -5.46500 | 2.46640 | H | -5.14830 | -8.89730 | 4.17130 |
| H | -6.59860 | -6.84870 | 3.49770 | H | -4.11890 | -10.10120 | 3.39250 |
| C | -4.78470 | -5.81570 | 3.85650 | H | -5.70770 | -9.75870 | 2.73630 |
| H | -4.53920 | -6.52560 | 4.63470 | | | | |
| C | -4.06300 | -4.68040 | 3.78860 | --- | | | |
| C | -4.24810 | -3.60740 | 2.72800 | | | | |
| H | -4.47270 | -2.65000 | 3.19820 | Compound **5.22** | | | |
| H | -5.05170 | -3.83190 | 2.02990 | This structure was assigned as ambiguous. | | | |
| H | -3.33700 | -3.49180 | 2.14100 | B3LYP/6-31g(d) | | | |
| C | -2.96010 | -4.41330 | 4.80370 | SMD implicit solvation in dichloromethane | | | |
| H | -3.20740 | -3.49660 | 5.33920 | was used. | | | |
| H | -2.95710 | -5.20160 | 5.55440 | | | | |
| C | -1.54120 | -4.28560 | 4.20850 | Electronic Energy: -1082.08673813 har- | | | |
| H | -1.46450 | -3.34480 | 3.66320 | tree. | | | |
| H | -0.80820 | -4.23070 | 5.01270 | Free Energy: -1081.663221 hartree. | | | |
| C | -1.12110 | -5.40530 | 3.25240 | | | | |
| O | -0.79440 | -5.14530 | 2.09530 | H | -4.55832 | 1.22990 | 0.57706 |
| O | -1.12170 | -6.63510 | 3.81100 | C | -4.32989 | 1.34793 | -0.48881 |
| C | -0.65510 | -7.76690 | 3.06730 | H | -5.05583 | 2.06356 | -0.90207 |
| H | -0.23880 | -7.42410 | 2.11920 | C | -4.55258 | -0.02597 | -1.19212 |
| C | 0.53150 | -8.39850 | 3.82960 | H | -5.56196 | -0.37447 | -0.95093 |
| H | 1.06810 | -9.05250 | 3.14250 | H | -4.52846 | 0.12717 | -2.28053 |
| H | 1.25790 | -7.63990 | 4.12540 | C | -3.49727 | -1.03049 | -0.81178 |
| O | 0.15310 | -9.20980 | 4.93870 | H | -2.50156 | -0.74332 | -1.14051 |
| C | -0.19630 | -8.50000 | 6.12200 | C | -3.60944 | -2.15767 | -0.09115 |
| H | 0.36560 | -8.93830 | 6.94700 | C | -4.90860 | -2.70563 | 0.44824 |
| H | 0.10040 | -7.45060 | 6.08020 | H | -5.05122 | -3.74948 | 0.13428 |
| C | -1.67040 | -8.62260 | 6.46150 | H | -5.78357 | -2.13749 | 0.12220 |
| C | -4.40460 | -8.86000 | 7.12340 | H | -4.90082 | -2.71236 | 1.54747 |
| C | -2.36940 | -7.52100 | 6.99620 | C | -2.39816 | -3.00520 | 0.27383 |
| C | -2.34060 | -9.85030 | 6.28060 | H | -2.47724 | -3.27585 | 1.33501 |
| C | -3.70590 | -9.96830 | 6.60670 | H | -2.44120 | -3.95798 | -0.27443 |
| C | -3.73540 | -7.63670 | 7.32070 | C | -1.01373 | -2.37701 | 0.04997 |
| H | -1.85860 | -6.58260 | 7.15370 | H | -0.24873 | -3.12489 | 0.29832 |
| H | -1.80470 | -10.69900 | 5.88000 | H | -0.84827 | -2.09197 | -0.99190 |
| H | -4.21640 | -10.90850 | 6.45680 | C | -0.76551 | -1.18948 | 0.96332 |
| H | -4.26930 | -6.78750 | 7.72220 | O | -1.06663 | -1.16740 | 2.14196 |
| H | -5.45250 | -8.94980 | 7.37130 | O | -0.14044 | -0.17964 | 0.31892 |
| C | -1.79850 | -8.75440 | 2.71140 | C | 0.17200 | 1.03210 | 1.07092 |
| H | -2.14200 | -9.20430 | 3.63920 | H | -0.15343 | 0.87485 | 2.10287 |
| C | -1.33190 | -9.87990 | 1.77360 | C | 1.68641 | 1.18832 | 1.07641 |
| H | -2.16090 | -10.53950 | 1.51530 | H | 1.97220 | 1.96909 | 1.79725 |
| H | -0.56630 | -10.49800 | 2.24250 | H | 2.13757 | 0.24559 | 1.41624 |
| H | -0.92270 | -9.48150 | 0.84460 | O | 2.13978 | 1.53170 | -0.22564 |

| | | | |
|---|---|---|---|
| C | 3.55274 | 1.63705 | -0.33177 |
| H | 3.72723 | 2.18717 | -1.26520 |
| H | 3.95796 | 2.25122 | 0.48729 |
| C | 4.27319 | 0.30021 | -0.38459 |
| C | 5.65872 | -2.13685 | -0.59152 |
| C | 5.59251 | 0.19020 | 0.07228 |
| C | 3.65175 | -0.82584 | -0.94025 |
| C | 4.33853 | -2.03756 | -1.03944 |
| C | 6.28444 | -1.01853 | -0.03481 |
| H | 6.08158 | 1.05585 | 0.51480 |
| H | 2.62288 | -0.74722 | -1.27988 |
| H | 3.84321 | -2.90489 | -1.46911 |
| H | 7.30858 | -1.08839 | 0.32331 |
| H | 6.19371 | -3.07970 | -0.67108 |
| C | -0.61030 | 2.21226 | 0.44700 |
| H | -0.22684 | 2.35576 | -0.56693 |
| C | -0.35926 | 3.50671 | 1.24722 |
| H | -0.93715 | 4.33169 | 0.81676 |
| H | 0.69705 | 3.79681 | 1.23149 |
| H | -0.66721 | 3.39611 | 2.29489 |
| C | -2.08220 | 1.87295 | 0.40860 |
| H | -2.48925 | 1.54257 | 1.36682 |
| C | -2.91658 | 1.87891 | -0.64440 |
| C | -2.53618 | 2.31169 | -2.03987 |
| H | -3.24371 | 3.06486 | -2.41398 |
| H | -2.58024 | 1.47062 | -2.74572 |
| H | -1.53220 | 2.73919 | -2.09920 |

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Compound **5.22**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1082.06004317 hartree.
Free Energy: -1081.637052 hartree.

| | | | |
|---|---|---|---|
| H | -4.53999 | 1.17647 | 0.56606 |
| C | -4.31040 | 1.30397 | -0.49799 |
| H | -5.05343 | 2.00296 | -0.90964 |
| C | -4.49454 | -0.07436 | -1.20396 |
| H | -5.50099 | -0.44287 | -0.98052 |
| H | -4.45800 | 0.07518 | -2.29286 |
| C | -3.42676 | -1.05743 | -0.80446 |
| H | -2.43139 | -0.74930 | -1.11375 |
| C | -3.53253 | -2.18206 | -0.08162 |
| C | -4.83174 | -2.75138 | 0.43559 |
| H | -4.95399 | -3.79575 | 0.11545 |
| H | -5.70907 | -2.19590 | 0.09631 |
| H | -4.84126 | -2.75990 | 1.53424 |
| C | -2.31697 | -3.00948 | 0.30884 |
| H | -2.39764 | -3.25438 | 1.37611 |
| H | -2.34918 | -3.97396 | -0.22045 |
| C | -0.93827 | -2.37098 | 0.08370 |
| H | -0.16652 | -3.10852 | 0.34198 |
| H | -0.77036 | -2.09150 | -0.95936 |
| C | -0.71160 | -1.17065 | 0.98867 |
| O | -1.03187 | -1.13384 | 2.15804 |
| O | -0.08074 | -0.16448 | 0.33497 |
| C | 0.19540 | 1.05606 | 1.07908 |
| H | -0.13966 | 0.89534 | 2.10843 |
| C | 1.70597 | 1.24995 | 1.09681 |
| H | 1.97073 | 2.02505 | 1.83407 |
| H | 2.17886 | 0.31106 | 1.41639 |
| O | 2.15375 | 1.63115 | -0.19415 |
| C | 3.56537 | 1.67345 | -0.32436 |
| H | 3.74480 | 2.22279 | -1.25681 |
| H | 4.01347 | 2.26381 | 0.49200 |
| C | 4.22111 | 0.30444 | -0.39562 |
| C | 5.47576 | -2.19593 | -0.63162 |
| C | 5.52677 | 0.11730 | 0.07081 |
| C | 3.54452 | -0.77646 | -0.97450 |
| C | 4.16764 | -2.01949 | -1.08834 |
| C | 6.15484 | -1.12345 | -0.05119 |
| H | 6.05736 | 0.94771 | 0.53306 |
| H | 2.52262 | -0.63584 | -1.31427 |
| H | 3.63119 | -2.85268 | -1.53543 |
| H | 7.16976 | -1.25424 | 0.31534 |
| H | 5.96062 | -3.16437 | -0.72218 |
| C | -0.60466 | 2.21350 | 0.43833 |
| H | -0.21622 | 2.34753 | -0.57498 |
| C | -0.38278 | 3.52525 | 1.21963 |
| H | -0.97971 | 4.32852 | 0.77641 |
| H | 0.66719 | 3.83642 | 1.19887 |
| H | -0.69220 | 3.42335 | 2.26757 |
| C | -2.06824 | 1.84226 | 0.39837 |
| H | -2.45937 | 1.46488 | 1.34534 |
| C | -2.91060 | 1.87003 | -0.64612 |
| C | -2.55428 | 2.37200 | -2.02518 |
| H | -3.24515 | 3.16979 | -2.33154 |
| H | -2.64699 | 1.57740 | -2.77797 |
| H | -1.53867 | 2.76905 | -2.08795 |

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Compound **5.22**
This structure was assigned as ambiguous.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1081.61359322 hartree.
Free Energy: -1081.184755 hartree.

| | | | |
|---|---|---|---|
| H | 4.46214 | 0.96138 | -0.12986 |
| C | 4.17428 | 0.92704 | 0.92689 |
| H | 4.94488 | 1.45678 | 1.50287 |
| C | 4.14493 | -0.55285 | 1.38024 |
| H | 3.99008 | -0.59082 | 2.46675 |
| H | 5.12280 | -1.00149 | 1.18577 |
| C | 3.03617 | -1.29482 | 0.68885 |
| H | 2.04205 | -0.95407 | 0.97598 |
| C | 3.12741 | -2.22545 | -0.26829 |
| C | 4.42021 | -2.79341 | -0.79157 |
| H | 4.38960 | -3.89017 | -0.77173 |
| H | 5.29465 | -2.47067 | -0.22333 |
| H | 4.56828 | -2.50323 | -1.83932 |
| C | 1.90166 | -2.79905 | -0.95056 |
| H | 2.07714 | -2.78467 | -2.03369 |
| H | 1.79532 | -3.85753 | -0.67778 |
| C | 0.58679 | -2.07649 | -0.67069 |
| H | -0.22600 | -2.58878 | -1.20086 |
| H | 0.32616 | -2.07687 | 0.39052 |
| C | 0.61183 | -0.65526 | -1.19354 |
| O | 1.12887 | -0.32687 | -2.23623 |
| O | -0.04294 | 0.18622 | -0.37687 |
| C | -0.22124 | 1.55539 | -0.79310 |
| H | 0.03959 | 1.63090 | -1.85332 |
| C | -1.69830 | 1.83894 | -0.60152 |
| H | -1.98484 | 1.55079 | 0.42046 |
| H | -1.90974 | 2.90908 | -0.73032 |
| O | -2.42006 | 1.08834 | -1.55827 |
| C | -3.79055 | 0.96781 | -1.24093 |
| H | -4.20791 | 1.93931 | -0.93636 |
| H | -4.28898 | 0.67730 | -2.17272 |
| C | -4.05729 | -0.07419 | -0.17160 |
| C | -4.56956 | -2.05727 | 1.73873 |
| C | -5.22748 | -0.03618 | 0.58949 |
| C | -3.14452 | -1.10981 | 0.03479 |
| C | -3.39668 | -2.09485 | 0.98675 |
| C | -5.48532 | -1.02540 | 1.53686 |
| H | -5.94053 | 0.77203 | 0.44091 |
| H | -2.22834 | -1.12152 | -0.54728 |
| H | -2.67508 | -2.89235 | 1.14135 |
| H | -6.39851 | -0.98640 | 2.12374 |
| H | -4.76634 | -2.82437 | 2.48186 |
| C | 0.68798 | 2.47559 | 0.04126 |
| H | 0.28805 | 2.49737 | 1.06209 |
| C | 0.68641 | 3.89929 | -0.53273 |
| H | 1.33259 | 4.54370 | 0.07049 |
| H | -0.31276 | 4.34457 | -0.54690 |
| H | 1.07440 | 3.89863 | -1.55793 |
| C | 2.08988 | 1.92484 | 0.04883 |
| H | 2.51363 | 1.75500 | -0.94364 |
| C | 2.83193 | 1.59540 | 1.11187 |
| C | 2.38026 | 1.73454 | 2.54435 |
| H | 2.00321 | 0.77865 | 2.93171 |
| H | 1.59152 | 2.47885 | 2.67303 |
| H | 3.22334 | 2.02423 | 3.18226 |

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Compound **5.22**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1082.06134085 hartree.
Free Energy: -1081.639408 hartree.

| | | | |
|---|---|---|---|
| H | -4.20276 | -1.93941 | 1.38111 |
| C | -3.79357 | -1.13304 | 2.00220 |
| H | -4.01840 | -1.39339 | 3.04753 |
| C | -4.54695 | 0.18355 | 1.66232 |
| H | -4.25662 | 0.97020 | 2.36606 |
| H | -5.61925 | 0.00334 | 1.83063 |
| C | -4.31734 | 0.60308 | 0.23624 |
| H | -4.56633 | -0.16356 | -0.49932 |
| C | -3.78895 | 1.74455 | -0.23218 |
| C | -3.38601 | 2.92816 | 0.61501 |
| H | -2.33027 | 3.18973 | 0.46110 |
| H | -3.53326 | 2.76245 | 1.68474 |
| H | -3.96894 | 3.81664 | 0.33374 |
| C | -3.51353 | 1.89490 | -1.71761 |
| H | -4.14320 | 1.21173 | -2.29621 |
| H | -3.74829 | 2.91585 | -2.04744 |
| C | -2.03819 | 1.60007 | -2.07662 |
| H | -1.86097 | 1.86612 | -3.12741 |
| H | -1.34582 | 2.18829 | -1.46853 |
| C | -1.71418 | 0.12284 | -1.93802 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O | -2.38593 | -0.76686 | -2.41820 | C | 3.89678 | 1.30310 | 1.81486 |
| O | -0.57091 | -0.07066 | -1.24122 | H | 4.17927 | 1.71612 | 2.79418 |
| C | -0.10483 | -1.43593 | -1.06310 | C | 4.53844 | -0.10899 | 1.69057 |
| H | -0.72967 | -2.08502 | -1.68472 | H | 4.17261 | -0.75380 | 2.49555 |
| C | 1.32109 | -1.49054 | -1.59789 | H | 5.61984 | 0.00937 | 1.85394 |
| H | 1.63428 | -2.54203 | -1.70320 | C | 4.29825 | -0.72188 | 0.33771 |
| H | 1.34147 | -1.03936 | -2.60313 | H | 4.71434 | -0.14617 | -0.49220 |
| O | 2.18967 | -0.79775 | -0.72373 | C | 3.60064 | -1.82739 | 0.02596 |
| C | 3.52204 | -0.72401 | -1.20069 | C | 2.95591 | -2.75292 | 1.03071 |
| H | 3.96437 | -1.73194 | -1.27369 | H | 1.86092 | -2.74225 | 0.94166 |
| H | 3.52267 | -0.30334 | -2.22258 | H | 3.20432 | -2.50222 | 2.06478 |
| C | 4.34880 | 0.14490 | -0.28129 | H | 3.27125 | -3.79071 | 0.85331 |
| C | 5.91799 | 1.80969 | 1.34508 | C | 3.38326 | -2.20312 | -1.42849 |
| C | 5.70608 | -0.12949 | -0.08329 | H | 4.07495 | -1.64988 | -2.07280 |
| C | 3.78127 | 1.25969 | 0.34763 | H | 3.58534 | -3.27285 | -1.57472 |
| C | 4.56113 | 2.08388 | 1.15885 | C | 1.94063 | -1.93180 | -1.92268 |
| C | 6.48953 | 0.70020 | 0.72057 | H | 1.83227 | -2.33581 | -2.93690 |
| H | 6.15410 | -1.00000 | -0.55830 | H | 1.20216 | -2.42422 | -1.28571 |
| H | 2.72481 | 1.46395 | 0.20559 | C | 1.64600 | -0.44701 | -2.00963 |
| H | 4.10833 | 2.94326 | 1.64690 | O | 2.27816 | 0.32759 | -2.70427 |
| H | 7.54256 | 0.47363 | 0.86609 | O | 0.59777 | -0.09540 | -1.23641 |
| H | 6.52425 | 2.45363 | 1.97672 | C | 0.16189 | 1.29675 | -1.24305 |
| C | -0.25610 | -1.82342 | 0.42546 | H | 0.78262 | 1.83850 | -1.96216 |
| H | 0.32838 | -1.09983 | 0.99979 | C | -1.27217 | 1.31312 | -1.75503 |
| C | 0.32485 | -3.22853 | 0.68978 | H | -1.57419 | 2.35023 | -1.96714 |
| H | 0.15980 | -3.50756 | 1.73516 | H | -1.31669 | 0.75912 | -2.70606 |
| H | 1.40244 | -3.26048 | 0.49932 | O | -2.13399 | 0.72478 | -0.79625 |
| H | -0.16186 | -3.98836 | 0.06475 | C | -3.47872 | 0.63885 | -1.24303 |
| C | -1.71181 | -1.77306 | 0.82445 | H | -3.89917 | 1.64494 | -1.40128 |
| H | -2.35974 | -2.40909 | 0.21808 | H | -3.51037 | 0.12489 | -2.21972 |
| C | -2.29210 | -1.05644 | 1.79961 | C | -4.30801 | -0.12213 | -0.23370 |
| C | -1.55813 | -0.12840 | 2.73770 | C | -5.89255 | -1.58959 | 1.56571 |
| H | -1.86346 | 0.91478 | 2.58296 | C | -5.66986 | 0.16813 | -0.08364 |
| H | -0.47314 | -0.17218 | 2.62137 | C | -3.74629 | -1.15438 | 0.52905 |
| H | -1.79448 | -0.37185 | 3.78283 | C | -4.53273 | -1.87996 | 1.42620 |
| ---------- | | | | C | -6.45976 | -0.56359 | 0.80606 |
| | | | | H | -6.11488 | 0.97282 | -0.66536 |
| Compound **5.22** | | | | H | -2.68915 | -1.37723 | 0.42242 |
| This structure was assigned as correct. | | | | H | -4.08226 | -2.67421 | 2.01645 |
| B3LYP/6-31g(d) | | | | H | -7.51518 | -0.32527 | 0.91178 |
| SMD implicit solvation in dichloromethane was used. | | | | H | -6.50410 | -2.15550 | 2.26375 |
| | | | | C | 0.36429 | 1.87756 | 0.17384 |
| | | | | H | -0.23664 | 1.27335 | 0.85919 |
| Electronic Energy: -1082.08882316 hartree. | | | | C | -0.14362 | 3.33313 | 0.24432 |
| | | | | H | 0.05195 | 3.74830 | 1.23871 |
| Free Energy: -1081.666951 hartree. | | | | H | -1.22211 | 3.39622 | 0.06353 |
| | | | | H | 0.36573 | 3.97167 | -0.48876 |
| H | 4.34361 | 1.95502 | 1.05382 | C | 1.82675 | 1.80829 | 0.55024 |

| | | | |
|---|---|---|---|
| H | 2.49939 | 2.22417 | -0.20297 |
| C | 2.38636 | 1.31139 | 1.66617 |
| C | 1.61829 | 0.72185 | 2.82466 |
| H | 1.91099 | -0.32015 | 3.00948 |
| H | 0.53561 | 0.74004 | 2.67802 |
| H | 1.83945 | 1.27321 | 3.74982 |

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Compound **5.22**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1081.61521713 hartree.
Free Energy: -1081.188180 hartree.

| | | | |
|---|---|---|---|
| H | -4.37540 | 1.46289 | 1.50936 |
| C | -3.90826 | 2.08323 | 0.73549 |
| H | -4.16753 | 3.12834 | 0.95199 |
| C | -4.51289 | 1.70340 | -0.63684 |
| H | -5.57605 | 1.97145 | -0.62688 |
| H | -4.04242 | 2.30794 | -1.41926 |
| C | -4.37250 | 0.23534 | -0.92381 |
| H | -5.09217 | -0.40959 | -0.41595 |
| C | -3.43602 | -0.35530 | -1.67658 |
| C | -2.33008 | 0.38531 | -2.38524 |
| H | -2.57110 | 1.43638 | -2.56023 |
| H | -2.10940 | -0.07811 | -3.35446 |
| H | -1.40678 | 0.35089 | -1.79074 |
| C | -3.39874 | -1.86007 | -1.81479 |
| H | -4.20078 | -2.31132 | -1.22228 |
| H | -3.56017 | -2.14306 | -2.86339 |
| C | -2.05246 | -2.46025 | -1.37484 |
| H | -2.10255 | -3.55228 | -1.43890 |
| H | -1.23562 | -2.11691 | -2.01323 |
| C | -1.76155 | -2.10111 | 0.06256 |
| O | -2.47929 | -2.39342 | 0.99223 |
| O | -0.61232 | -1.41616 | 0.17862 |
| C | -0.20072 | -0.97405 | 1.48863 |
| H | -0.82528 | -1.47276 | 2.23695 |
| C | 1.23291 | -1.42391 | 1.68420 |
| H | 1.51582 | -1.29169 | 2.73946 |
| H | 1.31294 | -2.49624 | 1.44917 |
| O | 2.07476 | -0.66861 | 0.84537 |
| C | 3.43005 | -1.02459 | 0.98725 |
| H | 3.77147 | -0.83064 | 2.01653 |
| H | 3.55353 | -2.10542 | 0.80692 |
| C | 4.27013 | -0.24373 | 0.00718 |
| C | 5.87740 | 1.13291 | -1.82647 |
| C | 3.70588 | 0.32580 | -1.13494 |
| C | 5.64436 | -0.11771 | 0.22480 |
| C | 6.44551 | 0.56283 | -0.68766 |
| C | 4.50694 | 1.01355 | -2.04543 |
| H | 2.63761 | 0.23141 | -1.30252 |
| H | 6.08793 | -0.55492 | 1.11683 |
| H | 7.51250 | 0.65481 | -0.50601 |
| H | 4.05717 | 1.45734 | -2.92915 |
| H | 6.49970 | 1.66984 | -2.53642 |
| C | -0.39749 | 0.54421 | 1.55724 |
| H | 0.16708 | 0.97214 | 0.72193 |
| C | 0.17335 | 1.11174 | 2.86357 |
| H | -0.02540 | 2.18622 | 2.91971 |
| H | 1.25667 | 0.96332 | 2.92037 |
| H | -0.29041 | 0.63776 | 3.73707 |
| C | -1.86414 | 0.87006 | 1.41946 |
| H | -2.54034 | 0.18068 | 1.92999 |
| C | -2.40807 | 1.91127 | 0.77765 |
| C | -1.61797 | 2.97507 | 0.06072 |
| H | -2.03326 | 3.16968 | -0.93534 |
| H | -0.56213 | 2.72081 | -0.05699 |
| H | -1.67468 | 3.92242 | 0.61274 |

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Compound **5.23**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +149.722305 kJ.

| | | | |
|---|---|---|---|
| C | -2.17760 | 3.77250 | 1.82010 |
| C | -1.30430 | 2.78440 | 1.65760 |
| O | -2.30140 | 3.11860 | -0.37370 |
| H | -2.34860 | 4.29450 | 2.74980 |
| H | -0.65190 | 2.36330 | 2.40770 |
| C | -2.85290 | 3.96990 | 0.55430 |
| C | -3.90350 | 4.79010 | 0.26740 |
| C | -4.57370 | 4.75680 | -1.07650 |
| C | -4.53020 | 5.65610 | 1.32120 |
| O | -5.12530 | 6.76230 | 0.82530 |
| O | -4.46600 | 5.43950 | 2.53420 |
| C | -5.78670 | 7.65670 | 1.70300 |
| H | -6.59070 | 7.15010 | 2.23840 |
| H | -6.22100 | 8.48000 | 1.13620 |

| | | | |
|---|---|---|---|
| H | -5.09040 | 8.07290 | 2.43210 |
| O | -5.78060 | 4.96870 | -1.22170 |
| C | -3.79120 | 4.48690 | -2.37320 |
| H | -2.72080 | 4.39830 | -2.20110 |
| H | -3.90740 | 5.38810 | -2.97510 |
| C | -4.33770 | 3.29430 | -3.19320 |
| H | -4.03090 | 3.40450 | -4.23330 |
| H | -5.42910 | 3.30700 | -3.20500 |
| C | -1.33640 | 2.30230 | 0.22800 |
| O | -0.09830 | 2.41230 | -0.40900 |
| C | 0.41950 | 3.72970 | -0.55200 |
| H | -0.24910 | 4.36200 | -1.13720 |
| H | 1.37320 | 3.68580 | -1.07760 |
| H | 0.59820 | 4.20720 | 0.41180 |
| C | -1.78270 | 0.82860 | 0.05960 |
| H | -1.68140 | 0.60450 | -1.00090 |
| C | -3.24330 | 0.59640 | 0.52570 |
| H | -3.85480 | 1.48420 | 0.38230 |
| H | -3.25930 | 0.42510 | 1.60280 |
| C | -3.85380 | 1.93760 | -2.71500 |
| H | -2.80220 | 1.74110 | -2.86860 |
| C | -4.62050 | 0.98820 | -2.14930 |
| H | -5.67030 | 1.17990 | -1.97550 |
| O | -0.93440 | -0.04040 | 0.78040 |
| H | -0.05030 | 0.19070 | 0.52960 |
| C | -4.10250 | -0.37780 | -1.72570 |
| H | -3.14310 | -0.56260 | -2.20940 |
| H | -4.77610 | -1.13750 | -2.12410 |
| C | -3.96340 | -0.55850 | -0.19730 |
| H | -4.95850 | -0.66650 | 0.23590 |
| H | -3.44400 | -1.49500 | 0.01100 |

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Compound **5.23**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +156.298828 kJ.

| | | | |
|---|---|---|---|
| C | -2.23720 | 3.66340 | 1.92230 |
| C | -1.35860 | 2.67380 | 1.79230 |
| O | -2.06710 | 3.19290 | -0.32190 |
| H | -2.52920 | 4.11470 | 2.85880 |
| H | -0.81700 | 2.17670 | 2.58280 |
| C | -2.71930 | 3.98280 | 0.59690 |
| C | -3.70400 | 4.84050 | 0.21940 |
| C | -4.07570 | 4.87470 | -1.21820 |
| C | -4.52350 | 5.64100 | 1.18570 |
| O | -5.40520 | 6.47510 | 0.58980 |
| O | -4.41350 | 5.58080 | 2.41210 |
| C | -6.22450 | 7.31450 | 1.38680 |
| H | -5.61710 | 7.98830 | 1.99260 |
| H | -6.85640 | 6.72370 | 2.05130 |
| H | -6.87040 | 7.91820 | 0.74940 |
| O | -3.28650 | 5.18540 | -2.11330 |
| C | -5.47780 | 4.38390 | -1.60820 |
| H | -6.07390 | 5.25000 | -1.89540 |
| H | -5.95350 | 3.95840 | -0.72470 |
| C | -5.49850 | 3.33510 | -2.74250 |
| H | -5.20670 | 3.80180 | -3.68440 |
| H | -6.52050 | 2.98150 | -2.88150 |
| C | -1.20790 | 2.30620 | 0.33400 |
| O | 0.10690 | 2.42370 | -0.12210 |
| C | 0.64330 | 3.74160 | -0.13860 |
| H | 0.07460 | 4.39720 | -0.79940 |
| H | 1.66680 | 3.70910 | -0.51130 |
| H | 0.66940 | 4.18610 | 0.85660 |
| C | -1.66110 | 0.86610 | -0.00940 |
| H | -1.52150 | 0.74880 | -1.08370 |
| C | -3.13840 | 0.60520 | 0.37880 |
| H | -3.74590 | 1.49440 | 0.22470 |
| H | -3.19720 | 0.40790 | 1.44990 |
| C | -4.58610 | 2.14250 | -2.50540 |
| H | -3.53110 | 2.31820 | -2.67180 |
| C | -4.99300 | 0.92600 | -2.10430 |
| H | -6.04110 | 0.74870 | -1.90990 |
| O | -0.85230 | -0.07800 | 0.66030 |
| H | 0.04160 | 0.19620 | 0.50180 |
| C | -4.06120 | -0.25260 | -1.88330 |
| H | -3.12260 | -0.07750 | -2.40900 |
| H | -4.50600 | -1.12650 | -2.36070 |
| C | -3.79760 | -0.55510 | -0.39320 |
| H | -4.74340 | -0.80610 | 0.08810 |
| H | -3.17270 | -1.44510 | -0.30440 |

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Compound **5.23**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1112.36025527 hartree.

Free Energy: -1112.038811 hartree.

| | | | |
|---|---|---|---|
| C | -2.24814 | 3.73771 | 1.90859 |
| C | -1.37473 | 2.72850 | 1.79963 |
| O | -2.07032 | 3.29903 | -0.33890 |
| H | -2.60231 | 4.23237 | 2.80019 |
| H | -0.85265 | 2.21699 | 2.59877 |
| C | -2.73402 | 4.06271 | 0.56679 |
| C | -3.75146 | 4.87960 | 0.16696 |
| C | -4.19676 | 4.85937 | -1.27841 |
| C | -4.47934 | 5.71041 | 1.13806 |
| O | -5.41729 | 6.45929 | 0.50571 |
| O | -4.28995 | 5.78065 | 2.34301 |
| C | -6.19911 | 7.33014 | 1.34188 |
| H | -5.55802 | 8.05406 | 1.85191 |
| H | -6.76085 | 6.75589 | 2.08379 |
| H | -6.88428 | 7.84416 | 0.66641 |
| O | -3.45784 | 5.21143 | -2.18200 |
| C | -5.59479 | 4.30618 | -1.56066 |
| H | -6.24517 | 5.15515 | -1.80840 |
| H | -6.00126 | 3.84340 | -0.65586 |
| C | -5.61991 | 3.29220 | -2.73023 |
| H | -5.36437 | 3.82374 | -3.65474 |
| H | -6.65107 | 2.93395 | -2.83504 |
| C | -1.20905 | 2.34283 | 0.35332 |
| O | 0.09057 | 2.42251 | -0.15035 |
| C | 0.81182 | 3.63590 | 0.09666 |
| H | 0.27547 | 4.50238 | -0.30437 |
| H | 1.76259 | 3.52821 | -0.42978 |
| H | 1.00397 | 3.78427 | 1.16556 |
| C | -1.68361 | 0.91687 | -0.03505 |
| H | -1.58938 | 0.89049 | -1.13028 |
| C | -3.11751 | 0.58987 | 0.38133 |
| H | -3.74007 | 1.48330 | 0.27552 |
| H | -3.10766 | 0.32768 | 1.44629 |
| C | -4.67864 | 2.12801 | -2.54511 |
| H | -3.62943 | 2.33303 | -2.76044 |
| C | -5.01513 | 0.90504 | -2.11825 |
| H | -6.06122 | 0.69249 | -1.88222 |
| O | -0.81514 | -0.04283 | 0.55680 |
| H | 0.08009 | 0.17262 | 0.24288 |
| C | -4.04116 | -0.22749 | -1.90955 |
| H | -3.10062 | 0.00262 | -2.42542 |
| H | -4.43544 | -1.13846 | -2.38174 |
| C | -3.75518 | -0.55597 | -0.42345 |
| H | -4.69749 | -0.83590 | 0.06587 |
| H | -3.10675 | -1.44019 | -0.37786 |

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Compound **5.23**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1112.33913821 hartree.
Free Energy: -1112.017324 hartree.

| | | | |
|---|---|---|---|
| C | -2.24548 | 3.74853 | 1.91935 |
| C | -1.38124 | 2.73083 | 1.81649 |
| O | -2.06111 | 3.29440 | -0.32656 |
| H | -2.60568 | 4.25515 | 2.80196 |
| H | -0.86939 | 2.20909 | 2.61515 |
| C | -2.72513 | 4.06861 | 0.57304 |
| C | -3.74193 | 4.88105 | 0.16838 |
| C | -4.17390 | 4.85381 | -1.28098 |
| C | -4.46881 | 5.70797 | 1.14445 |
| O | -5.44031 | 6.43049 | 0.52487 |
| O | -4.26151 | 5.79337 | 2.34361 |
| C | -6.20787 | 7.29084 | 1.37891 |
| H | -5.56081 | 8.02547 | 1.86536 |
| H | -6.72546 | 6.71064 | 2.14773 |
| H | -6.92527 | 7.78629 | 0.72396 |
| O | -3.41722 | 5.17124 | -2.17899 |
| C | -5.57735 | 4.31539 | -1.57349 |
| H | -6.21924 | 5.17108 | -1.81962 |
| H | -5.99338 | 3.85178 | -0.67312 |
| C | -5.58902 | 3.30534 | -2.74570 |
| H | -5.30874 | 3.83953 | -3.66097 |
| H | -6.61838 | 2.94899 | -2.87486 |
| C | -1.21760 | 2.33794 | 0.37106 |
| O | 0.09159 | 2.39967 | -0.12348 |
| C | 0.77855 | 3.64469 | 0.01956 |
| H | 0.24350 | 4.44693 | -0.49861 |
| H | 1.75503 | 3.49895 | -0.44610 |
| H | 0.91370 | 3.91449 | 1.07395 |
| C | -1.69632 | 0.91225 | -0.00687 |
| H | -1.58661 | 0.87533 | -1.10066 |
| C | -3.13907 | 0.60123 | 0.38978 |
| H | -3.75318 | 1.49765 | 0.26180 |
| H | -3.14617 | 0.34729 | 1.45636 |
| C | -4.65353 | 2.13945 | -2.54304 |
| H | -3.60031 | 2.34883 | -2.73103 |
| C | -5.00150 | 0.91510 | -2.13251 |
| H | -6.05333 | 0.70216 | -1.92418 |
| O | -0.84598 | -0.04546 | 0.60911 |

| | | | |
|---|---|---|---|
| H | 0.05354 | 0.15317 | 0.29998 |
| C | -4.03336 | -0.21987 | -1.90819 |
| H | -3.08645 | 0.00994 | -2.41252 |
| H | -4.41889 | -1.13029 | -2.38845 |
| C | -3.76656 | -0.54802 | -0.41798 |
| H | -4.71541 | -0.82693 | 0.05943 |
| H | -3.11700 | -1.43019 | -0.35860 |

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Compound **5.23**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1111.91257512 hartree.
Free Energy: -1111.586239 hartree.

| | | | |
|---|---|---|---|
| C | -2.21201 | 3.73504 | 1.87884 |
| C | -1.34702 | 2.72656 | 1.75929 |
| O | -2.00131 | 3.33888 | -0.37228 |
| H | -2.57501 | 4.21931 | 2.77273 |
| H | -0.83165 | 2.19572 | 2.55090 |
| C | -2.68438 | 4.07432 | 0.52984 |
| C | -3.71091 | 4.86800 | 0.13463 |
| C | -4.14891 | 4.82755 | -1.30203 |
| C | -4.47668 | 5.65168 | 1.11577 |
| O | -5.44316 | 6.35743 | 0.50103 |
| O | -4.28533 | 5.71248 | 2.31321 |
| C | -6.24955 | 7.17328 | 1.35382 |
| H | -5.63471 | 7.92094 | 1.85973 |
| H | -6.76360 | 6.56094 | 2.09814 |
| H | -6.97261 | 7.65854 | 0.69935 |
| O | -3.38739 | 5.09045 | -2.20886 |
| C | -5.56214 | 4.33050 | -1.57770 |
| H | -6.18364 | 5.19547 | -1.83803 |
| H | -5.98227 | 3.88716 | -0.66944 |
| C | -5.57493 | 3.30792 | -2.72583 |
| H | -5.28588 | 3.82034 | -3.64982 |
| H | -6.60058 | 2.94528 | -2.85339 |
| C | -1.18671 | 2.36193 | 0.30684 |
| O | 0.11037 | 2.40773 | -0.17906 |
| C | 0.82623 | 3.60546 | 0.10398 |
| H | 0.26667 | 4.48402 | -0.23320 |
| H | 1.76229 | 3.54072 | -0.45188 |
| H | 1.04353 | 3.69629 | 1.17383 |
| C | -1.71751 | 0.96993 | -0.07858 |
| H | -1.64466 | 0.94164 | -1.17661 |
| C | -3.15142 | 0.72392 | 0.36686 |
| H | -3.74773 | 1.62645 | 0.18796 |
| H | -3.14086 | 0.54535 | 1.44843 |
| C | -4.64529 | 2.14866 | -2.48289 |
| H | -3.58011 | 2.35240 | -2.61129 |
| C | -5.02259 | 0.92501 | -2.10714 |
| H | -6.08470 | 0.71941 | -1.95422 |
| O | -0.89297 | -0.01808 | 0.50324 |
| H | 0.00907 | 0.15411 | 0.18741 |
| C | -4.07025 | -0.21094 | -1.84717 |
| H | -3.12331 | -0.01267 | -2.36202 |
| H | -4.47338 | -1.13335 | -2.28226 |
| C | -3.80683 | -0.45908 | -0.35014 |
| H | -4.75755 | -0.68689 | 0.14670 |
| H | -3.17120 | -1.34557 | -0.24086 |

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Compound **5.23**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1112.35722722 hartree.
Free Energy: -1112.036977 hartree.

| | | | |
|---|---|---|---|
| C | -2.21495 | 3.83341 | 1.82994 |
| C | -1.33520 | 2.83107 | 1.71284 |
| O | -2.21250 | 3.26009 | -0.38939 |
| H | -2.50431 | 4.36844 | 2.72123 |
| H | -0.73771 | 2.38353 | 2.49711 |
| C | -2.83385 | 4.05208 | 0.52002 |
| C | -3.91800 | 4.81836 | 0.18680 |
| C | -4.68266 | 4.66433 | -1.08919 |
| C | -4.52653 | 5.68307 | 1.23887 |
| O | -5.05322 | 6.80022 | 0.70053 |
| O | -4.52713 | 5.46994 | 2.44068 |
| C | -5.70643 | 7.69030 | 1.62212 |
| H | -6.52803 | 7.18216 | 2.13453 |
| H | -6.09228 | 8.50874 | 1.01290 |
| H | -4.99790 | 8.07247 | 2.36249 |
| O | -5.90612 | 4.73271 | -1.04317 |
| C | -3.99945 | 4.44711 | -2.43637 |
| H | -2.91848 | 4.33945 | -2.33650 |
| H | -4.18416 | 5.37809 | -2.99137 |
| C | -4.61254 | 3.26530 | -3.23092 |
| H | -4.40874 | 3.43414 | -4.29701 |
| H | -5.69990 | 3.29074 | -3.10249 |

| | | | |
|---|---|---|---|
| C | -1.28494 | 2.35034 | 0.28789 |
| O | -0.03336 | 2.40261 | -0.32508 |
| C | 0.70922 | 3.62103 | -0.19356 |
| H | 0.14753 | 4.47239 | -0.59292 |
| H | 1.61571 | 3.48024 | -0.78616 |
| H | 0.98465 | 3.81907 | 0.84857 |
| C | -1.78203 | 0.90355 | 0.02467 |
| H | -1.72558 | 0.79882 | -1.06665 |
| C | -3.20650 | 0.62506 | 0.50329 |
| H | -3.81216 | 1.52595 | 0.37339 |
| H | -3.17161 | 0.41251 | 1.57875 |
| C | -4.05297 | 1.92590 | -2.82954 |
| H | -3.00775 | 1.76134 | -3.10136 |
| C | -4.69488 | 0.95526 | -2.16873 |
| H | -5.73669 | 1.10749 | -1.87620 |
| O | -0.90017 | -0.01981 | 0.65355 |
| H | -0.01959 | 0.14136 | 0.27291 |
| C | -4.06102 | -0.35083 | -1.75818 |
| H | -3.08134 | -0.44109 | -2.24410 |
| H | -4.66515 | -1.19067 | -2.13118 |
| C | -3.90398 | -0.53599 | -0.22729 |
| H | -4.89806 | -0.66272 | 0.22138 |
| H | -3.36045 | -1.47209 | -0.04608 |

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Compound **5.23**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1112.33590002 hartree.
Free Energy: -1112.013929 hartree.

| | | | |
|---|---|---|---|
| C | -2.17407 | 3.82823 | 1.86549 |
| C | -1.32926 | 2.79678 | 1.73992 |
| O | -2.19962 | 3.25150 | -0.35669 |
| H | -2.45902 | 4.37268 | 2.75249 |
| H | -0.75279 | 2.31256 | 2.51782 |
| C | -2.79518 | 4.06570 | 0.55915 |
| C | -3.87243 | 4.83637 | 0.22520 |
| C | -4.66384 | 4.59635 | -1.03233 |
| C | -4.43278 | 5.76680 | 1.24197 |
| O | -5.19540 | 6.71736 | 0.66251 |
| O | -4.20706 | 5.75289 | 2.44097 |
| C | -5.79451 | 7.65844 | 1.56335 |
| H | -6.43282 | 7.14516 | 2.28736 |
| H | -6.38728 | 8.32356 | 0.93474 |
| H | -5.02693 | 8.22044 | 2.10296 |
| O | -5.87833 | 4.51618 | -0.94214 |
| C | -3.99317 | 4.46217 | -2.39793 |
| H | -2.90885 | 4.37178 | -2.30914 |
| H | -4.19910 | 5.41471 | -2.90850 |
| C | -4.59532 | 3.30185 | -3.22835 |
| H | -4.38297 | 3.49137 | -4.28927 |
| H | -5.68255 | 3.32473 | -3.10397 |
| C | -1.29251 | 2.32826 | 0.30988 |
| O | -0.03076 | 2.36931 | -0.30073 |
| C | 0.69354 | 3.59660 | -0.21218 |
| H | 0.12077 | 4.42319 | -0.64616 |
| H | 1.60581 | 3.44537 | -0.79245 |
| H | 0.95605 | 3.84102 | 0.82395 |
| C | -1.79509 | 0.88829 | 0.03545 |
| H | -1.72598 | 0.78938 | -1.05633 |
| C | -3.22782 | 0.62082 | 0.49413 |
| H | -3.82344 | 1.52729 | 0.35671 |
| H | -3.20656 | 0.40219 | 1.56843 |
| C | -4.04028 | 1.95525 | -2.84343 |
| H | -2.99708 | 1.78506 | -3.12048 |
| C | -4.68624 | 0.98750 | -2.18376 |
| H | -5.72430 | 1.15061 | -1.88619 |
| O | -0.92957 | -0.04217 | 0.67251 |
| H | -0.04536 | 0.10945 | 0.29972 |
| C | -4.06421 | -0.32733 | -1.78326 |
| H | -3.08182 | -0.41867 | -2.26400 |
| H | -4.66836 | -1.15918 | -2.17348 |
| C | -3.92005 | -0.53235 | -0.25309 |
| H | -4.91806 | -0.66339 | 0.18537 |
| H | -3.37660 | -1.46864 | -0.07526 |

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Compound **5.23**
This structure was assigned as ambiguous.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1111.90775091 hartree.
Free Energy: -1111.582640 hartree.

| | | | |
|---|---|---|---|
| C | -2.33723 | 3.72044 | 1.75061 |
| C | -1.44301 | 2.73123 | 1.72071 |
| O | -2.00864 | 3.23602 | -0.46006 |
| H | -2.73882 | 4.23742 | 2.61030 |
| H | -0.95281 | 2.25180 | 2.55975 |
| C | -2.73250 | 4.01656 | 0.36391 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -3.68877 | 4.87604 | -0.07639 | C | -5.31460 | 4.92020 | -1.57500 |
| C | -4.03327 | 5.19466 | -1.48822 | C | -5.44750 | 4.69380 | -0.27140 |
| C | -4.43664 | 5.63648 | 0.97099 | O | -4.07200 | 6.50320 | -0.47510 |
| O | -5.75761 | 5.53285 | 0.80492 | H | -5.76640 | 4.32960 | -2.35810 |
| O | -3.93026 | 6.24368 | 1.88996 | H | -6.02140 | 3.90750 | 0.19510 |
| C | -6.55060 | 6.27604 | 1.73311 | C | -4.47460 | 6.08710 | -1.71970 |
| H | -6.32336 | 7.34245 | 1.66206 | C | -4.12170 | 6.76960 | -2.84150 |
| H | -6.36867 | 5.93390 | 2.75465 | C | -3.29660 | 7.99960 | -2.67990 |
| H | -7.58682 | 6.09184 | 1.45201 | C | -4.61180 | 6.40740 | -4.21080 |
| O | -4.74373 | 6.16149 | -1.71428 | O | -3.99240 | 7.08220 | -5.20500 |
| C | -3.54024 | 4.35467 | -2.65150 | O | -5.47670 | 5.55980 | -4.44140 |
| H | -2.59670 | 3.85907 | -2.43393 | C | -4.33510 | 6.81210 | -6.55440 |
| H | -3.39673 | 5.04799 | -3.48552 | H | -5.39030 | 7.01970 | -6.73670 |
| C | -4.59725 | 3.30792 | -3.06889 | H | -3.74390 | 7.43950 | -7.22130 |
| H | -4.22227 | 2.78339 | -3.95443 | H | -4.13770 | 5.76870 | -6.80390 |
| H | -5.50378 | 3.84871 | -3.36955 | O | -2.24200 | 8.02390 | -2.04160 |
| C | -1.21598 | 2.29512 | 0.29789 | C | -3.82130 | 9.32860 | -3.24310 |
| O | 0.09297 | 2.32522 | -0.14879 | H | -3.08850 | 9.69590 | -3.96140 |
| C | 0.80341 | 3.53130 | 0.11460 | H | -4.74190 | 9.15610 | -3.79950 |
| H | 0.99993 | 3.64950 | 1.18567 | C | -4.07440 | 10.40390 | -2.16480 |
| H | 1.74993 | 3.45223 | -0.42122 | H | -3.14190 | 10.63730 | -1.64780 |
| H | 0.25124 | 4.40088 | -0.25630 | H | -4.39200 | 11.32550 | -2.65270 |
| C | -1.74587 | 0.88887 | -0.04788 | C | -4.67710 | 5.72790 | 0.51690 |
| H | -1.79122 | 0.86325 | -1.14857 | O | -3.75730 | 5.17070 | 1.40770 |
| C | -3.12172 | 0.60456 | 0.53417 | C | -2.66530 | 4.48470 | 0.80850 |
| H | -3.72676 | 1.51829 | 0.49060 | H | -2.01540 | 4.08980 | 1.58910 |
| H | -2.98259 | 0.36339 | 1.59379 | H | -2.99560 | 3.64450 | 0.19720 |
| C | -4.94699 | 2.30844 | -2.00162 | H | -2.06570 | 5.15320 | 0.18900 |
| H | -5.49254 | 2.69162 | -1.13573 | C | -5.60020 | 6.67160 | 1.31560 |
| C | -4.67316 | 1.00338 | -2.06105 | H | -6.28000 | 7.12720 | 0.59570 |
| H | -4.12636 | 0.61811 | -2.92537 | C | -4.77020 | 7.76400 | 2.02440 |
| O | -0.85479 | -0.08611 | 0.44550 | H | -4.31140 | 7.34550 | 2.92070 |
| H | 0.01916 | 0.12801 | 0.08021 | H | -3.92850 | 8.06220 | 1.39870 |
| C | -5.05762 | 0.00081 | -1.00959 | C | -5.13950 | 10.02410 | -1.14820 |
| H | -5.56992 | -0.84708 | -1.48152 | H | -6.06100 | 9.62360 | -1.54640 |
| H | -5.77132 | 0.46275 | -0.31562 | C | -5.01770 | 10.19320 | 0.17990 |
| C | -3.85985 | -0.52653 | -0.20105 | H | -4.10820 | 10.61950 | 0.57980 |
| H | -4.22613 | -1.26955 | 0.51455 | O | -6.37520 | 5.95540 | 2.25440 |
| H | -3.16504 | -1.05584 | -0.86519 | H | -5.76300 | 5.41650 | 2.73640 |
| --- | | | | C | -6.09330 | 9.84460 | 1.19470 |
| | | | | H | -6.52320 | 10.77700 | 1.56240 |
| Compound **5.24** | | | | H | -6.90850 | 9.31610 | 0.69980 |
| This structure was assigned as incorrect. | | | | C | -5.57140 | 9.02640 | 2.39570 |
| | | | | H | -6.40920 | 8.74780 | 3.03660 |
| Molecular Mechanics (OPLS-2005), gas phase. | | | | H | -4.93360 | 9.66930 | 3.00340 |
| Energy: +143.085236 kJ. | | | | --- | | | |

Compound **5.24**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +148.252704 kJ.

| | | | |
|---|---|---|---|
| C | -5.19390 | 4.97300 | -1.61640 |
| C | -5.29950 | 4.77350 | -0.30890 |
| O | -4.24500 | 6.78190 | -0.58130 |
| H | -5.55900 | 4.29220 | -2.37120 |
| H | -5.75600 | 3.92630 | 0.18030 |
| C | -4.54240 | 6.25000 | -1.81550 |
| C | -4.25350 | 6.86650 | -3.00000 |
| C | -3.61680 | 8.22840 | -3.08690 |
| C | -4.65000 | 6.23400 | -4.30120 |
| O | -3.75560 | 6.43870 | -5.29160 |
| O | -5.65400 | 5.53380 | -4.45810 |
| C | -4.01590 | 5.92730 | -6.58700 |
| H | -3.20390 | 6.19600 | -7.26240 |
| H | -4.09890 | 4.84000 | -6.56700 |
| H | -4.94280 | 6.34030 | -6.98720 |
| O | -3.72230 | 8.94910 | -4.08260 |
| C | -2.78890 | 8.83740 | -1.94310 |
| H | -2.56420 | 8.11740 | -1.16110 |
| H | -1.82060 | 9.09200 | -2.37400 |
| C | -3.40970 | 10.12900 | -1.36290 |
| H | -2.68890 | 10.61310 | -0.70360 |
| H | -3.61010 | 10.83930 | -2.16670 |
| C | -4.68030 | 5.92440 | 0.44470 |
| O | -3.64110 | 5.51280 | 1.28390 |
| C | -2.49720 | 4.96510 | 0.64050 |
| H | -1.75540 | 4.69740 | 1.39270 |
| H | -2.73560 | 4.06190 | 0.07820 |
| H | -2.03530 | 5.68630 | -0.03470 |
| C | -5.70910 | 6.70090 | 1.30420 |
| H | -6.37920 | 7.20880 | 0.61020 |
| C | -4.99680 | 7.72000 | 2.21980 |
| H | -4.65290 | 7.21570 | 3.12350 |
| H | -4.07970 | 8.06580 | 1.74220 |
| C | -4.70490 | 9.88770 | -0.61210 |
| H | -5.47780 | 9.35120 | -1.14430 |
| C | -4.92200 | 10.25730 | 0.66000 |
| H | -4.15030 | 10.78220 | 1.20520 |
| O | -6.49470 | 5.83230 | 2.09610 |
| H | -5.88970 | 5.31020 | 2.60300 |
| C | -6.16810 | 9.89950 | 1.44550 |
| H | -6.61800 | 10.81640 | 1.82820 |
| H | -6.90760 | 9.45590 | 0.77790 |
| C | -5.85960 | 8.93810 | 2.61240 |
| H | -6.79110 | 8.59870 | 3.06800 |
| H | -5.33260 | 9.49400 | 3.38870 |

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Compound **5.24**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1112.36161338 hartree.
Free Energy: -1112.040062 hartree.

| | | | |
|---|---|---|---|
| C | -5.25629 | 4.92794 | -1.60581 |
| C | -5.40807 | 4.67823 | -0.29894 |
| O | -3.94307 | 6.46046 | -0.52052 |
| H | -5.70970 | 4.42519 | -2.44606 |
| H | -6.02047 | 3.91236 | 0.16004 |
| C | -4.38392 | 6.09624 | -1.74536 |
| C | -4.07785 | 6.84735 | -2.84974 |
| C | -3.31923 | 8.13794 | -2.68793 |
| C | -4.53233 | 6.41734 | -4.18386 |
| O | -3.94177 | 7.16172 | -5.15178 |
| O | -5.29816 | 5.50184 | -4.44623 |
| C | -4.30410 | 6.83271 | -6.50478 |
| H | -5.38239 | 6.93424 | -6.65481 |
| H | -3.76692 | 7.54515 | -7.13216 |
| H | -3.99842 | 5.81129 | -6.74744 |
| O | -2.28299 | 8.19791 | -2.04454 |
| C | -3.93237 | 9.41031 | -3.27880 |
| H | -3.23271 | 9.80194 | -4.02740 |
| H | -4.87077 | 9.19018 | -3.79541 |
| C | -4.16810 | 10.49211 | -2.19893 |
| H | -3.21808 | 10.73021 | -1.70788 |
| H | -4.49463 | 11.40183 | -2.72455 |
| C | -4.62720 | 5.68123 | 0.51374 |
| O | -3.70848 | 5.16012 | 1.41553 |
| C | -2.79761 | 4.17311 | 0.91510 |
| H | -2.13178 | 3.93529 | 1.74721 |
| H | -3.32133 | 3.26370 | 0.59785 |
| H | -2.20680 | 4.56765 | 0.08179 |
| C | -5.51587 | 6.67213 | 1.31255 |
| H | -6.24262 | 7.07830 | 0.60309 |
| C | -4.69135 | 7.80464 | 1.94366 |
| H | -4.17439 | 7.40038 | 2.82325 |

| | | | |
|---|---|---|---|
| H | -3.91290 | 8.11299 | 1.23890 |
| C | -5.19989 | 10.09928 | -1.17230 |
| H | -6.12052 | 9.66165 | -1.56755 |
| C | -5.07483 | 10.24974 | 0.15113 |
| H | -4.15577 | 10.69202 | 0.54431 |
| O | -6.28465 | 5.95395 | 2.27270 |
| H | -5.64510 | 5.56755 | 2.89677 |
| C | -6.10480 | 9.84804 | 1.17633 |
| H | -6.57327 | 10.74830 | 1.60318 |
| H | -6.91300 | 9.29174 | 0.68378 |
| C | -5.51975 | 9.03237 | 2.35271 |
| H | -6.33853 | 8.72481 | 3.01558 |
| H | -4.87241 | 9.69252 | 2.94555 |

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Compound **5.24**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1112.33967323 hartree.
Free Energy: -1112.017997 hartree.

| | | | |
|---|---|---|---|
| C | -5.28648 | 4.92833 | -1.60993 |
| C | -5.44581 | 4.68555 | -0.30255 |
| O | -3.97660 | 6.46251 | -0.51738 |
| H | -5.73490 | 4.43344 | -2.45779 |
| H | -6.07069 | 3.93487 | 0.16395 |
| C | -4.40501 | 6.09135 | -1.74716 |
| C | -4.08581 | 6.83452 | -2.85005 |
| C | -3.30860 | 8.11481 | -2.67788 |
| C | -4.53275 | 6.39390 | -4.18311 |
| O | -3.98616 | 7.17262 | -5.15481 |
| O | -5.26028 | 5.45010 | -4.44630 |
| C | -4.33846 | 6.81707 | -6.49941 |
| H | -5.42042 | 6.87696 | -6.64556 |
| H | -3.82454 | 7.53880 | -7.13517 |
| H | -4.00697 | 5.80048 | -6.72694 |
| O | -2.28445 | 8.15568 | -2.01977 |
| C | -3.89753 | 9.40011 | -3.26866 |
| H | -3.18474 | 9.78350 | -4.00880 |
| H | -4.83300 | 9.19678 | -3.79790 |
| C | -4.12291 | 10.47246 | -2.17844 |
| H | -3.17169 | 10.67667 | -1.67535 |
| H | -4.42437 | 11.39924 | -2.68971 |
| C | -4.65869 | 5.68704 | 0.50753 |
| O | -3.74063 | 5.15117 | 1.41083 |
| C | -2.75460 | 4.26606 | 0.87491 |
| H | -2.14263 | 3.95485 | 1.72351 |
| H | -3.21319 | 3.38371 | 0.41196 |
| H | -2.12763 | 4.78160 | 0.14051 |
| C | -5.53960 | 6.66759 | 1.32287 |
| H | -6.27823 | 7.07489 | 0.62591 |
| C | -4.70837 | 7.79956 | 1.94572 |
| H | -4.18591 | 7.39416 | 2.82138 |
| H | -3.93436 | 8.10417 | 1.23468 |
| C | -5.17165 | 10.08620 | -1.16605 |
| H | -6.09312 | 9.66017 | -1.57202 |
| C | -5.06167 | 10.23463 | 0.15759 |
| H | -4.14174 | 10.66556 | 0.56052 |
| O | -6.29114 | 5.94010 | 2.28671 |
| H | -5.63983 | 5.54191 | 2.88880 |
| C | -6.10603 | 9.84464 | 1.17235 |
| H | -6.57511 | 10.74864 | 1.59003 |
| H | -6.91309 | 9.29312 | 0.67224 |
| C | -5.53764 | 9.02618 | 2.35546 |
| H | -6.36259 | 8.71582 | 3.00896 |
| H | -4.89557 | 9.68450 | 2.95631 |

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Compound **5.24**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1111.91213246 hartree.
Free Energy: -1111.585452 hartree.

| | | | |
|---|---|---|---|
| C | -5.22995 | 4.92647 | -1.60183 |
| C | -5.39716 | 4.69913 | -0.29807 |
| O | -3.91172 | 6.45438 | -0.51720 |
| H | -5.67481 | 4.41796 | -2.44324 |
| H | -6.01805 | 3.94700 | 0.17303 |
| C | -4.34849 | 6.09529 | -1.73707 |
| C | -4.04474 | 6.84509 | -2.83103 |
| C | -3.31477 | 8.14256 | -2.65579 |
| C | -4.50564 | 6.42536 | -4.16521 |
| O | -3.94835 | 7.18908 | -5.12313 |
| O | -5.25336 | 5.50403 | -4.42457 |
| C | -4.32871 | 6.86493 | -6.46244 |
| H | -5.41178 | 6.94032 | -6.58326 |
| H | -3.82564 | 7.59315 | -7.09753 |
| H | -4.00488 | 5.85298 | -6.71593 |
| O | -2.31511 | 8.22742 | -1.97227 |

| | | | |
|---|---|---|---|
| C | -3.93099 | 9.39225 | -3.27343 |
| H | -3.23319 | 9.77878 | -4.02450 |
| H | -4.86618 | 9.15276 | -3.78680 |
| C | -4.17867 | 10.45734 | -2.19473 |
| H | -3.23329 | 10.70469 | -1.70093 |
| H | -4.53059 | 11.36610 | -2.70052 |
| C | -4.61587 | 5.71092 | 0.50083 |
| O | -3.72643 | 5.19045 | 1.42111 |
| C | -2.84250 | 4.19317 | 0.92023 |
| H | -2.12901 | 3.98995 | 1.71975 |
| H | -3.38093 | 3.27253 | 0.66978 |
| H | -2.30360 | 4.55568 | 0.03893 |
| C | -5.50324 | 6.71602 | 1.25463 |
| H | -6.18305 | 7.14625 | 0.51043 |
| C | -4.66586 | 7.81048 | 1.91332 |
| H | -4.15398 | 7.37280 | 2.77889 |
| H | -3.88937 | 8.13171 | 1.21082 |
| C | -5.19400 | 10.02495 | -1.17078 |
| H | -6.10446 | 9.56097 | -1.56066 |
| C | -5.06991 | 10.19609 | 0.14631 |
| H | -4.15747 | 10.65951 | 0.53121 |
| O | -6.31767 | 6.02683 | 2.18142 |
| H | -5.71425 | 5.63618 | 2.83574 |
| C | -6.09802 | 9.80741 | 1.17329 |
| H | -6.56926 | 10.71256 | 1.58015 |
| H | -6.89956 | 9.23606 | 0.68953 |
| C | -5.49645 | 9.01763 | 2.34759 |
| H | -6.30127 | 8.69168 | 3.01678 |
| H | -4.85295 | 9.68911 | 2.92911 |

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Compound **5.24**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1112.33539140 hartree.
Free Energy: -1112.013582 hartree.

| | | | |
|---|---|---|---|
| C | -5.20335 | 4.99865 | -1.66879 |
| C | -5.34856 | 4.74591 | -0.36353 |
| O | -4.11200 | 6.69667 | -0.57653 |
| H | -5.60147 | 4.45063 | -2.50913 |
| H | -5.88816 | 3.93054 | 0.09973 |
| C | -4.45690 | 6.25261 | -1.81638 |
| C | -4.16784 | 6.93682 | -2.96474 |
| C | -3.66257 | 8.34004 | -3.06043 |
| C | -4.56431 | 6.29562 | -4.26111 |
| O | -3.61266 | 6.47370 | -5.19701 |
| O | -5.57587 | 5.64848 | -4.46349 |
| C | -3.92684 | 5.96078 | -6.49971 |
| H | -3.07176 | 6.21689 | -7.12583 |
| H | -4.06886 | 4.87696 | -6.46540 |
| H | -4.83734 | 6.42739 | -6.88471 |
| O | -3.94327 | 8.99351 | -4.05748 |
| C | -2.84049 | 9.00678 | -1.95809 |
| H | -2.63449 | 8.33356 | -1.12604 |
| H | -1.88484 | 9.27262 | -2.42921 |
| C | -3.52214 | 10.30851 | -1.45995 |
| H | -2.81648 | 10.86648 | -0.83297 |
| H | -3.73744 | 10.92221 | -2.34386 |
| C | -4.66913 | 5.81428 | 0.45298 |
| O | -3.66012 | 5.36102 | 1.30503 |
| C | -2.64305 | 4.53893 | 0.73132 |
| H | -1.93740 | 4.33415 | 1.53862 |
| H | -3.04926 | 3.59342 | 0.35262 |
| H | -2.12460 | 5.06203 | -0.07934 |
| C | -5.63058 | 6.64942 | 1.33441 |
| H | -6.36775 | 7.09028 | 0.65692 |
| C | -4.89358 | 7.74137 | 2.12760 |
| H | -4.45147 | 7.27031 | 3.01473 |
| H | -4.05725 | 8.11814 | 1.53238 |
| C | -4.78127 | 10.02129 | -0.68959 |
| H | -5.55323 | 9.47236 | -1.23357 |
| C | -4.99829 | 10.31976 | 0.59418 |
| H | -4.22981 | 10.86572 | 1.14780 |
| O | -6.37365 | 5.77761 | 2.18021 |
| H | -5.73606 | 5.40139 | 2.80997 |
| C | -6.19065 | 9.86210 | 1.39169 |
| H | -6.72610 | 10.72036 | 1.82251 |
| H | -6.90299 | 9.35919 | 0.72494 |
| C | -5.78465 | 8.91954 | 2.55348 |
| H | -6.68724 | 8.54367 | 3.05207 |
| H | -5.23728 | 9.50699 | 3.30291 |

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Compound **5.24**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1112.35748717 hartree.
Free Energy: -1112.036226 hartree.

| | | | |
|---|---|---|---|
| C | -5.00027 | 4.91290 | -1.56760 |
| C | -5.18114 | 4.64643 | -0.26998 |
| O | -3.91881 | 6.59214 | -0.44219 |
| H | -5.34892 | 4.33960 | -2.41536 |
| H | -5.72022 | 3.81581 | 0.16680 |
| C | -4.24172 | 6.16083 | -1.68551 |
| C | -3.93523 | 6.83053 | -2.83778 |
| C | -3.15886 | 8.07698 | -3.02326 |
| C | -4.38434 | 6.18874 | -4.12382 |
| O | -5.28698 | 6.95173 | -4.76257 |
| O | -4.00839 | 5.10676 | -4.53463 |
| C | -5.71599 | 6.47040 | -6.05081 |
| H | -6.43230 | 7.20802 | -6.41469 |
| H | -4.86634 | 6.40009 | -6.73561 |
| H | -6.19349 | 5.49090 | -5.96009 |
| O | -2.87177 | 8.41973 | -4.17176 |
| C | -2.69779 | 8.95477 | -1.86753 |
| H | -2.58368 | 8.39291 | -0.93973 |
| H | -1.71718 | 9.34022 | -2.16694 |
| C | -3.64093 | 10.17316 | -1.63450 |
| H | -3.09171 | 10.91413 | -1.04141 |
| H | -3.84796 | 10.63320 | -2.61081 |
| C | -4.56251 | 5.73360 | 0.57228 |
| O | -3.63420 | 5.32902 | 1.51832 |
| C | -2.60468 | 4.43261 | 1.07943 |
| H | -1.96660 | 4.26581 | 1.94958 |
| H | -3.01842 | 3.47464 | 0.74424 |
| H | -2.00852 | 4.87690 | 0.27529 |
| C | -5.61727 | 6.59236 | 1.31830 |
| H | -6.31390 | 6.95229 | 0.55636 |
| C | -4.99612 | 7.77114 | 2.08273 |
| H | -4.59429 | 7.38961 | 3.02990 |
| H | -4.14363 | 8.16036 | 1.51899 |
| C | -4.91500 | 9.80783 | -0.92385 |
| H | -5.58258 | 9.12254 | -1.44952 |
| C | -5.23740 | 10.20597 | 0.31154 |
| H | -4.56098 | 10.88577 | 0.83683 |
| O | -6.39350 | 5.74909 | 2.16610 |
| H | -5.78781 | 5.42275 | 2.85487 |
| C | -6.41748 | 9.71068 | 1.10364 |
| H | -7.03959 | 10.55398 | 1.43710 |
| H | -7.05562 | 9.08912 | 0.46257 |
| C | -5.98281 | 8.91680 | 2.36205 |
| H | -6.87579 | 8.52450 | 2.86558 |
| H | -5.50777 | 9.61166 | 3.06733 |

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Compound **5.24**

This structure was assigned as ambiguous.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1111.90697610 hartree.
Free Energy: -1111.583177 hartree.

| | | | |
|---|---|---|---|
| C | -5.16644 | 5.16026 | -1.73937 |
| C | -5.30111 | 4.82277 | -0.45823 |
| O | -4.00879 | 6.74347 | -0.55434 |
| H | -5.57081 | 4.65527 | -2.60665 |
| H | -5.84201 | 3.98277 | -0.04066 |
| C | -4.37610 | 6.39849 | -1.80584 |
| C | -4.09331 | 7.12295 | -2.91768 |
| C | -3.32031 | 8.38116 | -3.03652 |
| C | -4.63956 | 6.61869 | -4.22113 |
| O | -4.09428 | 5.44337 | -4.57262 |
| O | -5.47189 | 7.18723 | -4.88289 |
| C | -4.59108 | 4.88536 | -5.79382 |
| H | -4.39248 | 5.55971 | -6.62977 |
| H | -4.05667 | 3.94572 | -5.92871 |
| H | -5.66660 | 4.70489 | -5.72358 |
| O | -3.11888 | 8.83986 | -4.15112 |
| C | -2.78093 | 9.12885 | -1.83203 |
| H | -2.63101 | 8.48163 | -0.96726 |
| H | -1.81380 | 9.53120 | -2.14778 |
| C | -3.70696 | 10.31125 | -1.46201 |
| H | -3.14460 | 11.00795 | -0.83108 |
| H | -3.96107 | 10.84460 | -2.38711 |
| C | -4.61599 | 5.84474 | 0.41236 |
| O | -3.65555 | 5.35410 | 1.27464 |
| C | -2.70296 | 4.47147 | 0.69044 |
| H | -1.93847 | 4.30077 | 1.44914 |
| H | -3.16333 | 3.51559 | 0.41752 |
| H | -2.23875 | 4.92026 | -0.19382 |
| C | -5.60965 | 6.65719 | 1.25698 |
| H | -6.32174 | 7.09683 | 0.55062 |
| C | -4.91799 | 7.74353 | 2.07834 |
| H | -4.46865 | 7.27029 | 2.95982 |
| H | -4.09673 | 8.17018 | 1.49398 |
| C | -4.94413 | 9.87323 | -0.73209 |
| H | -5.60466 | 9.17637 | -1.25437 |
| C | -5.24183 | 10.24444 | 0.51333 |
| H | -4.56396 | 10.92760 | 1.03193 |
| O | -6.36128 | 5.77370 | 2.06691 |
| H | -5.73465 | 5.38331 | 2.69911 |
| C | -6.38585 | 9.71015 | 1.32520 |

| | | | |
|---|---|---|---|
| H | -6.98872 | 10.53300 | 1.72917 |
| H | -7.04966 | 9.12119 | 0.68174 |
| C | -5.87748 | 8.85647 | 2.50484 |
| H | -6.73347 | 8.42347 | 3.03619 |
| H | -5.36050 | 9.51203 | 3.21612 |

---

Compound **5.25**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +90.034286 kJ.

| | | | |
|---|---|---|---|
| C | -9.39880 | -6.33260 | 29.69310 |
| C | -10.09790 | -7.46630 | 28.95630 |
| C | -11.28410 | -9.55220 | 27.46910 |
| C | -10.95640 | -8.39790 | 29.61020 |
| C | -9.88860 | -7.56570 | 27.56380 |
| C | -10.53000 | -8.56550 | 26.80970 |
| C | -11.48060 | -9.47320 | 28.85630 |
| C | -11.29940 | -8.27700 | 31.10450 |
| H | -9.28070 | -6.83070 | 27.05590 |
| C | -10.47120 | -8.54400 | 25.29240 |
| H | -12.08260 | -10.23300 | 29.32870 |
| H | -11.75860 | -10.34640 | 26.91090 |
| H | -10.12470 | -5.73150 | 30.24120 |
| H | -8.92770 | -5.65330 | 28.98160 |
| O | -8.40530 | -6.80780 | 30.57400 |
| H | -7.83540 | -7.38210 | 30.08420 |
| H | -10.71340 | -7.46160 | 31.51530 |
| C | -10.85490 | -9.50790 | 31.91820 |
| C | -11.40690 | -7.48850 | 24.63910 |
| H | -10.74290 | -9.53740 | 24.93310 |
| H | -9.44220 | -8.38260 | 24.96890 |
| C | -12.75710 | -7.26170 | 25.36700 |
| O | -11.68250 | -7.88280 | 23.29940 |
| H | -10.89130 | -6.52650 | 24.62750 |
| H | -13.05790 | -8.17190 | 25.88500 |
| H | -13.54660 | -7.08360 | 24.63580 |
| C | -12.73540 | -6.05140 | 26.32740 |
| C | -10.83550 | -7.55490 | 22.30990 |
| O | -9.77600 | -6.94440 | 22.44000 |
| C | -11.31380 | -8.03640 | 20.95000 |
| H | -10.61490 | -7.72830 | 20.17260 |
| H | -12.29300 | -7.61520 | 20.72460 |
| H | -11.38870 | -9.12330 | 20.94040 |
| C | -13.66360 | -6.18320 | 27.52800 |
| H | -13.00400 | -5.14950 | 25.77640 |
| H | -11.72360 | -5.87280 | 26.68650 |
| C | -13.20010 | -6.01590 | 28.78600 |
| C | -15.11840 | -6.46140 | 27.18460 |
| H | -15.79220 | -6.31490 | 28.02640 |
| H | -15.23710 | -7.48590 | 26.83230 |
| H | -15.44840 | -5.78970 | 26.39190 |
| C | -13.21230 | -6.48760 | 31.34190 |
| H | -12.16010 | -5.76480 | 28.91670 |
| H | -13.88870 | -6.24600 | 32.16240 |
| H | -12.35730 | -5.82590 | 31.48240 |
| C | -12.78060 | -7.98170 | 31.53180 |
| C | -13.82040 | -8.91160 | 30.84260 |
| C | -12.68150 | -8.34730 | 33.05530 |
| H | -14.83190 | -8.71960 | 31.20050 |
| H | -13.61130 | -9.96720 | 31.00980 |
| H | -13.85150 | -8.75610 | 29.76510 |
| O | -13.95040 | -8.60760 | 33.61510 |
| C | -12.05130 | -7.26840 | 33.96780 |
| H | -10.90270 | -10.42640 | 31.33410 |
| C | -11.82490 | -9.62140 | 33.09860 |
| H | -9.82090 | -9.39620 | 32.24660 |
| H | -11.30270 | -9.74610 | 34.04810 |
| H | -12.44310 | -10.51040 | 32.96820 |
| H | -14.42340 | -9.16350 | 33.01470 |
| H | -12.65020 | -6.35980 | 34.01650 |
| H | -11.04820 | -6.98520 | 33.65160 |
| H | -11.96670 | -7.63210 | 34.99240 |
| C | -14.00200 | -6.06090 | 30.07520 |
| H | -14.89980 | -6.66510 | 29.96350 |
| H | -14.36060 | -5.04410 | 30.23820 |

---

Compound **5.25**
This structure was assigned as ambiguous.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: +103.425819 kJ.

| | | | |
|---|---|---|---|
| C | -9.34390 | -6.14280 | 30.08490 |
| C | -9.87880 | -7.18780 | 29.11710 |
| C | -10.72360 | -9.07240 | 27.18910 |
| C | -10.65180 | -8.31290 | 29.52470 |
| C | -9.62930 | -6.97800 | 27.74660 |
| C | -10.12540 | -7.86810 | 26.77560 |
| C | -10.97530 | -9.29340 | 28.55530 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -11.18470 | -8.44580 | 30.95990 | H | -9.74310 | -9.61070 | 32.10810 |
| H | -9.11640 | -6.07950 | 27.43480 | H | -11.37350 | -10.23590 | 33.69180 |
| C | -10.08250 | -7.47760 | 25.30530 | H | -12.31030 | -10.98340 | 32.42220 |
| H | -11.50300 | -10.19090 | 28.83870 | H | -14.41120 | -9.82200 | 32.33060 |
| H | -11.07140 | -9.78780 | 26.45740 | H | -13.07180 | -7.02210 | 33.86170 |
| H | -8.53470 | -5.58370 | 29.61300 | H | -11.38180 | -7.44300 | 33.63780 |
| H | -8.89660 | -6.62020 | 30.95720 | H | -12.37410 | -8.33600 | 34.76800 |
| O | -10.33640 | -5.22730 | 30.48480 | C | -14.05410 | -6.37240 | 29.85450 |
| H | -10.81540 | -4.95830 | 29.71430 | H | -14.91630 | -7.00860 | 29.65590 |
| H | -10.74320 | -7.64600 | 31.54560 | H | -14.46330 | -5.39010 | 30.08520 |
| C | -10.72880 | -9.73860 | 31.65970 | | | | |
| C | -11.47680 | -7.27800 | 24.63650 | --- | | | |
| H | -9.48050 | -8.20260 | 24.75640 | | | | |
| H | -9.53830 | -6.53670 | 25.22030 | Compound **5.25** | | | |
| C | -12.64820 | -6.86690 | 25.56680 | This structure was assigned as correct. | | | |
| O | -11.88320 | -8.51290 | 24.05370 | B3LYP/6-31g(d) | | | |
| H | -11.38330 | -6.52710 | 23.84990 | SMD implicit solvation in methanol was used. | | | |
| H | -12.82870 | -7.67360 | 26.27560 | | | | |
| H | -13.56430 | -6.81410 | 24.97740 | | | | |
| C | -12.48600 | -5.52390 | 26.31380 | Electronic Energy: -1275.24684975 hartree. | | | |
| C | -11.52660 | -8.82120 | 22.79580 | | | | |
| O | -10.82390 | -8.13440 | 22.05670 | Free Energy: -1274.734319 hartree. | | | |
| C | -12.07980 | -10.16340 | 22.34610 | | | | |
| H | -13.16820 | -10.15850 | 22.39870 | C | 0.83229 | -2.24379 | -1.84965 |
| H | -11.70100 | -10.96020 | 22.98570 | C | 0.26359 | -1.65792 | -0.57221 |
| H | -11.78150 | -10.37000 | 21.31820 | C | -0.92263 | -0.73345 | 1.78227 |
| C | -13.38620 | -5.42560 | 27.54110 | C | 1.08395 | -1.08277 | 0.43096 |
| H | -12.67970 | -4.69550 | 25.63120 | C | -1.12463 | -1.70681 | -0.39263 |
| H | -11.46140 | -5.38560 | 26.65070 | C | -1.74791 | -1.19823 | 0.75348 |
| C | -13.23470 | -6.27900 | 28.57680 | C | 0.46216 | -0.69149 | 1.62503 |
| C | -14.43330 | -4.32750 | 27.47860 | C | 2.58037 | -0.91151 | 0.23445 |
| H | -15.13200 | -4.35190 | 28.31250 | H | -1.73759 | -2.13075 | -1.18641 |
| H | -15.01960 | -4.42600 | 26.5647 | C | -3.25086 | -1.07330 | 0.85854 |
| H | -13.95220 | -3.34930 | 27.46920 | H | 1.06389 | -0.32006 | 2.44756 |
| C | -13.30360 | -6.87020 | 31.12510 | H | -1.36602 | -0.38028 | 2.71069 |
| H | -12.49160 | -7.04260 | 28.46470 | H | 1.44950 | -1.51993 | -2.39013 |
| H | -14.05790 | -6.77910 | 31.90670 | H | 0.00820 | -2.53106 | -2.51650 |
| H | -12.53720 | -6.15130 | 31.40830 | O | 1.69408 | -3.37174 | -1.61841 |
| C | -12.73420 | -8.33340 | 31.21110 | H | 1.17053 | -4.03629 | -1.13888 |
| C | -13.57680 | -9.27370 | 30.30000 | H | 2.82184 | -1.34324 | -0.73633 |
| C | -12.77710 | -8.87000 | 32.68720 | C | 3.43777 | -1.68311 | 1.27975 |
| H | -14.63720 | -9.22980 | 30.54780 | C | -3.82984 | 0.09552 | 0.02305 |
| H | -13.26720 | -10.31510 | 30.37700 | H | -3.52486 | -0.88870 | 1.90382 |
| H | -13.50870 | -8.99940 | 29.24950 | H | -3.75038 | -1.99728 | 0.54515 |
| O | -14.06830 | -9.31090 | 33.04760 | C | -3.06308 | 1.42455 | 0.14276 |
| C | -12.37740 | -7.85790 | 33.78790 | O | -5.19291 | 0.34086 | 0.50538 |
| H | -10.65440 | -10.57360 | 30.96360 | H | -3.91461 | -0.19799 | -1.02583 |
| C | -11.80300 | -10.06010 | 32.70460 | H | -2.48966 | 1.43247 | 1.07583 |

| | | | |
|---|---|---|---|
| H | -3.79666 | 2.23367 | 0.22055 |
| C | -2.12950 | 1.67530 | -1.07702 |
| C | -6.19462 | -0.40052 | -0.00014 |
| O | -6.03837 | -1.27142 | -0.84215 |
| C | -7.51749 | -0.01481 | 0.60495 |
| H | -8.31904 | -0.59461 | 0.14453 |
| H | -7.70165 | 1.05514 | 0.46028 |
| H | -7.49970 | -0.20379 | 1.68423 |
| C | -0.81133 | 2.36913 | -0.77775 |
| H | -2.69390 | 2.27360 | -1.80930 |
| H | -1.91215 | 0.72423 | -1.57288 |
| C | 0.33970 | 1.82262 | -1.21175 |
| C | -0.91083 | 3.69019 | -0.05409 |
| H | 0.06186 | 4.16051 | 0.11418 |
| H | -1.40180 | 3.57902 | 0.92232 |
| H | -1.52690 | 4.39759 | -0.62892 |
| C | 2.90495 | 1.36135 | -1.09178 |
| H | 0.26339 | 0.88256 | -1.75867 |
| H | 3.80578 | 1.95661 | -1.29142 |
| H | 2.79834 | 0.68062 | -1.94671 |
| C | 3.20765 | 0.53494 | 0.19326 |
| C | 2.87835 | 1.37968 | 1.43826 |
| C | 4.74990 | 0.14024 | 0.24163 |
| H | 3.41394 | 2.33576 | 1.40583 |
| H | 3.14951 | 0.87879 | 2.37416 |
| H | 1.81232 | 1.61321 | 1.48793 |
| O | 5.59719 | 1.25557 | 0.56618 |
| C | 5.31509 | -0.36807 | -1.09227 |
| H | 2.96587 | -1.65711 | 2.26699 |
| C | 4.81220 | -0.97625 | 1.31330 |
| H | 3.51015 | -2.73799 | 0.99257 |
| H | 5.64763 | -1.65782 | 1.12132 |
| H | 4.99283 | -0.52532 | 2.29609 |
| H | 5.41382 | 1.51472 | 1.48443 |
| H | 5.27832 | 0.39990 | -1.87081 |
| H | 4.78690 | -1.25385 | -1.45610 |
| H | 6.36583 | -0.64364 | -0.94595 |
| C | 1.73913 | 2.38231 | -1.12626 |
| H | 1.83468 | 3.08800 | -0.29490 |
| H | 1.91368 | 2.98428 | -2.03362 |

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Compound **5.25**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in methanol was used.

Electronic Energy: -1274.71499892 hartree.
Free Energy: -1274.193197 hartree.

| | | | |
|---|---|---|---|
| C | -0.81659 | -2.34076 | 1.83737 |
| C | -0.23545 | -1.72500 | 0.58236 |
| C | 0.96349 | -0.73914 | -1.73009 |
| C | -1.04683 | -1.14751 | -0.41779 |
| C | 1.15257 | -1.74305 | 0.42780 |
| C | 1.77804 | -1.21220 | -0.70170 |
| C | -0.42074 | -0.72506 | -1.59454 |
| C | -2.54610 | -1.02439 | -0.25274 |
| H | 1.76350 | -2.16908 | 1.22355 |
| C | 3.27652 | -1.08105 | -0.79607 |
| H | -1.02029 | -0.36121 | -2.42285 |
| H | 1.41639 | -0.36745 | -2.64664 |
| H | -0.04871 | -2.95522 | 2.32292 |
| H | -1.65433 | -3.00018 | 1.59218 |
| O | -1.33461 | -1.38657 | 2.76273 |
| H | -0.58372 | -0.87897 | 3.10978 |
| H | -2.79786 | -1.45160 | 0.72024 |
| C | -3.33784 | -1.81120 | -1.33000 |
| C | 3.82419 | 0.12418 | -0.00621 |
| H | 3.55782 | -0.92319 | -1.84382 |
| H | 3.77828 | -1.98897 | -0.44607 |
| C | 3.00080 | 1.40327 | -0.17511 |
| O | 5.15908 | 0.40117 | -0.49732 |
| H | 3.91454 | -0.12505 | 1.05600 |
| H | 2.48042 | 1.37558 | -1.13916 |
| H | 3.68675 | 2.25551 | -0.20988 |
| C | 2.00310 | 1.57862 | 0.99212 |
| C | 6.15525 | -0.37644 | -0.05610 |
| O | 5.99543 | -1.27793 | 0.74230 |
| C | 7.46776 | 0.00999 | -0.67055 |
| H | 8.26728 | -0.59105 | -0.23839 |
| H | 7.65989 | 1.07269 | -0.50057 |
| H | 7.42188 | -0.15457 | -1.75132 |
| C | 0.67911 | 2.22798 | 0.65121 |
| H | 2.50300 | 2.18306 | 1.76373 |
| H | 1.80031 | 0.60844 | 1.45657 |
| C | -0.45673 | 1.70491 | 1.13455 |
| C | 0.76402 | 3.50148 | -0.14706 |
| H | -0.20826 | 3.97565 | -0.29858 |
| H | 1.20883 | 3.32092 | -1.13366 |
| H | 1.41634 | 4.22450 | 0.36088 |
| C | -2.99219 | 1.23895 | 1.02779 |
| H | -0.37368 | 0.78906 | 1.72005 |
| H | -3.91529 | 1.81601 | 1.17656 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.90213 | 0.57298 | 1.89518 | H | -1.02668 | 2.37547 | 1.07327 |
| C | -3.20946 | 0.39413 | -0.24675 | H | -2.87653 | -0.11568 | 1.44741 |
| C | -2.84975 | 1.23090 | -1.48014 | C | -3.02359 | -2.22455 | 1.06920 |
| C | -4.72283 | -0.03263 | -0.35394 | C | 3.82860 | 0.37183 | -0.06168 |
| H | -3.42245 | 2.16564 | -1.48244 | H | 4.01025 | -0.89656 | 1.66570 |
| H | -3.05445 | 0.70559 | -2.42006 | H | 3.53700 | 0.75241 | 2.03875 |
| H | -1.79132 | 1.50671 | -1.47404 | C | 2.76200 | 1.00532 | -0.95073 |
| O | -5.57411 | 1.05824 | -0.69544 | O | 4.26361 | -0.78958 | -0.81637 |
| C | -5.30732 | -0.56670 | 0.95374 | H | 4.69260 | 1.03334 | 0.04951 |
| H | -3.40155 | -2.86875 | -1.05537 | H | 2.02203 | 0.23044 | -1.16081 |
| C | -4.72063 | -1.13726 | -1.42724 | H | 3.22953 | 1.25153 | -1.91078 |
| H | -2.81877 | -1.76425 | -2.29238 | C | 2.09039 | 2.26155 | -0.37510 |
| H | -5.54912 | -1.83548 | -1.27390 | C | 5.47793 | -1.28376 | -0.54717 |
| H | -4.86316 | -0.68159 | -2.41346 | O | 6.21909 | -0.81034 | 0.29083 |
| H | -5.36699 | 1.33109 | -1.60349 | C | 5.79636 | -2.46913 | -1.40938 |
| H | -5.30186 | 0.19415 | 1.73916 | H | 5.81574 | -2.16070 | -2.45878 |
| H | -4.77065 | -1.44738 | 1.31684 | H | 5.01707 | -3.22812 | -1.29800 |
| H | -6.34724 | -0.85826 | 0.77342 | H | 6.76483 | -2.87930 | -1.12447 |
| C | -1.84965 | 2.26918 | 1.06421 | C | 0.67010 | 2.52493 | -0.87420 |
| H | -1.95345 | 2.97421 | 0.23400 | H | 2.70778 | 3.13399 | -0.62131 |
| H | -2.01274 | 2.86392 | 1.97597 | H | 2.07208 | 2.22495 | 0.72182 |
| --- | | | | C | -0.20160 | 1.52857 | -1.10557 |
| | | | | C | 0.35404 | 3.98880 | -1.04369 |
| Compound **5.25** | | | | H | -0.70237 | 4.18637 | -1.23695 |
| This structure was assigned as incorrect. | | | | H | 0.94006 | 4.41995 | -1.86565 |
| M06-2X/6-31g(d) | | | | H | 0.63798 | 4.53863 | -0.13740 |
| SMD implicit solvation in methanol was used. | | | | C | -2.78859 | 1.03049 | -1.01125 |
| | | | | H | 0.13562 | 0.51414 | -0.90326 |
| | | | | H | -3.63089 | 1.20876 | -1.69466 |
| Electronic Energy: -1274.71265419 hartree. | | | | H | -2.98386 | 1.62625 | -0.11470 |
| | | | | C | -2.84435 | -0.47105 | -0.64914 |
| Free Energy: -1274.190369 hartree. | | | | C | -2.13864 | -1.29946 | -1.72895 |
| | | | | C | -4.34609 | -0.94366 | -0.56304 |
| C | -1.22772 | 1.25082 | 2.65936 | H | -2.55482 | -1.06960 | -2.71664 |
| C | -0.37750 | 0.21646 | 1.96067 | H | -2.24148 | -2.37820 | -1.56248 |
| C | 1.37803 | -1.53235 | 0.67565 | H | -1.06922 | -1.07719 | -1.77181 |
| C | -0.90336 | -0.78098 | 1.11887 | O | -4.95999 | -1.04269 | -1.84563 |
| C | 1.00496 | 0.35652 | 2.08230 | C | -5.25084 | 0.01597 | 0.20888 |
| C | 1.90360 | -0.45765 | 1.39749 | H | -2.32323 | -3.02980 | 0.82842 |
| C | 0.00002 | -1.69367 | 0.55532 | C | -4.26756 | -2.30245 | 0.16221 |
| C | -2.37910 | -0.84221 | 0.79984 | H | -3.26918 | -2.32638 | 2.13052 |
| H | 1.39245 | 1.17020 | 2.69421 | H | -5.18910 | -2.50317 | 0.71695 |
| C | 3.36139 | -0.07483 | 1.34324 | H | -4.15988 | -3.10229 | -0.57912 |
| H | -0.37642 | -2.52186 | -0.03860 | H | -4.54050 | -1.77242 | -2.32918 |
| H | 2.04723 | -2.22081 | 0.16325 | H | -5.32618 | 0.98724 | -0.28768 |
| H | -0.63112 | 1.71578 | 3.45498 | H | -4.90740 | 0.17394 | 1.23488 |
| H | -2.11047 | 0.80765 | 3.13034 | H | -6.25554 | -0.41694 | 0.25543 |
| O | -1.70534 | 2.25266 | 1.76241 | C | -1.56207 | 1.61078 | -1.74896 |

| | | | |
|---|---|---|---|
| H | -1.48067 | 1.09889 | -2.71891 |
| H | -1.80422 | 2.65103 | -1.98900 |

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Compound **5.25**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
SMD implicit solvation in methanol was used.

Electronic Energy: -1275.24263359 hartree.
Free Energy: -1274.729206 hartree.

| | | | |
|---|---|---|---|
| C | -1.30551 | 0.58460 | 3.01495 |
| C | -0.43708 | -0.18701 | 2.03964 |
| C | 1.34358 | -1.63564 | 0.43617 |
| C | -0.95335 | -0.98752 | 0.99279 |
| C | 0.94995 | -0.05747 | 2.18413 |
| C | 1.86276 | -0.70810 | 1.34843 |
| C | -0.03538 | -1.76992 | 0.27099 |
| C | -2.42784 | -0.97152 | 0.63669 |
| H | 1.32936 | 0.60929 | 2.95689 |
| C | 3.32374 | -0.31273 | 1.37437 |
| H | -0.40001 | -2.46933 | -0.47430 |
| H | 2.01526 | -2.21580 | -0.19227 |
| H | -0.70374 | 0.82705 | 3.90167 |
| H | -2.15564 | -0.01396 | 3.35501 |
| O | -1.88042 | 1.78865 | 2.47909 |
| H | -1.15740 | 2.29622 | 2.07232 |
| H | -2.92600 | -0.36394 | 1.39394 |
| C | -3.11871 | -2.36361 | 0.65488 |
| C | 3.84834 | 0.34111 | 0.06429 |
| H | 3.97275 | -1.16887 | 1.59419 |
| H | 3.47980 | 0.40336 | 2.18865 |
| C | 2.82717 | 1.09600 | -0.79337 |
| O | 4.34844 | -0.70856 | -0.83328 |
| H | 4.69984 | 0.97812 | 0.31542 |
| H | 2.08160 | 0.37166 | -1.12751 |
| H | 3.34438 | 1.44414 | -1.69594 |
| C | 2.13504 | 2.29488 | -0.10921 |
| C | 5.60786 | -1.14918 | -0.66410 |
| O | 6.36178 | -0.73178 | 0.20131 |
| C | 5.95547 | -2.21043 | -1.67300 |
| H | 5.82307 | -1.82059 | -2.68807 |
| H | 5.28185 | -3.06685 | -1.55746 |
| H | 6.98801 | -2.53385 | -1.53206 |
| C | 0.76897 | 2.67245 | -0.69920 |
| H | 2.80162 | 3.16448 | -0.16287 |
| H | 2.00468 | 2.09414 | 0.96166 |
| C | -0.16091 | 1.73054 | -0.94834 |
| C | 0.57637 | 4.15348 | -0.91713 |
| H | -0.42424 | 4.41611 | -1.27117 |
| H | 1.30238 | 4.53674 | -1.64887 |
| H | 0.75884 | 4.71006 | 0.01351 |
| C | -2.74172 | 1.22340 | -0.83996 |
| H | 0.11328 | 0.70042 | -0.73902 |
| H | -3.61232 | 1.56634 | -1.41449 |
| H | -2.84056 | 1.66178 | 0.15805 |
| C | -2.87487 | -0.32897 | -0.73925 |
| C | -2.20730 | -0.99409 | -1.95950 |
| C | -4.40967 | -0.75323 | -0.72058 |
| H | -2.61119 | -0.58040 | -2.89072 |
| H | -2.36012 | -2.07861 | -1.98526 |
| H | -1.12943 | -0.81825 | -1.97549 |
| O | -5.03145 | -0.62440 | -2.01083 |
| C | -5.29537 | 0.10435 | 0.19363 |
| H | -2.45451 | -3.13572 | 0.25358 |
| C | -4.38445 | -2.22228 | -0.22356 |
| H | -3.35315 | -2.65660 | 1.68413 |
| H | -5.30455 | -2.46734 | 0.31774 |
| H | -4.33909 | -2.89782 | -1.08562 |
| H | -4.61754 | -1.26772 | -2.60983 |
| H | -5.31842 | 1.15145 | -0.12260 |
| H | -4.97316 | 0.06784 | 1.23784 |
| H | -6.32074 | -0.28049 | 0.14858 |
| C | -1.53137 | 1.88492 | -1.56000 |
| H | -1.49294 | 1.49505 | -2.58830 |
| H | -1.78311 | 2.94645 | -1.66424 |

---

Compound **5.25**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1275.20963297 hartree.
Free Energy: -1274.695189 hartree.

| | | | |
|---|---|---|---|
| C | -0.70617 | -0.52947 | 2.69772 |
| C | -0.22728 | -1.09975 | 1.37647 |
| C | 0.83985 | -2.04509 | -1.02468 |
| C | -1.10253 | -1.36462 | 0.29453 |
| C | 1.15119 | -1.27523 | 1.21232 |
| C | 1.71813 | -1.66461 | -0.00654 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.54001 | -1.92533 | -0.86122 | C | -4.87962 | -1.69765 | -0.29443 |
| C | -2.58301 | -1.03488 | 0.36855 | H | -3.58768 | -2.84668 | 1.08457 |
| H | 1.80594 | -1.04155 | 2.05028 | H | -5.70617 | -2.00746 | 0.35303 |
| C | 3.20399 | -1.55111 | -0.26266 | H | -5.13250 | -2.05061 | -1.30221 |
| H | -1.18447 | -2.22575 | -1.68041 | H | -5.42149 | 0.02187 | -2.13043 |
| H | 1.23696 | -2.40441 | -1.97163 | H | -5.14579 | 1.53013 | 1.02742 |
| H | 0.10885 | -0.60716 | 3.43305 | H | -4.69080 | 0.04642 | 1.88450 |
| H | -1.55227 | -1.09757 | 3.09983 | H | -6.29060 | 0.18888 | 1.13381 |
| O | -1.15786 | 0.82271 | 2.59817 | C | -1.58828 | 2.24720 | -0.92990 |
| H | -0.59569 | 1.27419 | 1.94386 | H | -1.69064 | 2.14363 | -2.01965 |
| H | -2.76936 | -0.65546 | 1.37375 | H | -1.70279 | 3.31830 | -0.73225 |
| C | -3.51410 | -2.26402 | 0.16000 | ---------- | | | |
| C | 3.73606 | -0.09664 | -0.14005 | | | | |
| H | 3.41954 | -1.89202 | -1.28221 | Compound **5.25** | | | |
| H | 3.78829 | -2.17904 | 0.41997 | This structure was assigned as correct. | | | |
| C | 2.82840 | 0.99466 | -0.75052 | B3LYP/6-31g(d) | | | |
| O | 5.02177 | -0.03336 | -0.82337 | Gas phase. | | | |
| H | 3.93286 | 0.12391 | 0.91256 | | | | |
| H | 2.07806 | 0.53615 | -1.39967 | Electronic Energy: -1275.21219177 hartree. | | | |
| H | 3.44444 | 1.63394 | -1.39142 | | | | |
| C | 2.14283 | 1.86421 | 0.33622 | Free Energy: -1274.698678 hartree. | | | |
| C | 6.11424 | -0.41792 | -0.12177 | | | | |
| O | 6.08258 | -0.81939 | 1.02189 | C | -0.80275 | -2.28111 | 1.91910 |
| C | 7.36395 | -0.26944 | -0.95919 | C | -0.24707 | -1.74161 | 0.61351 |
| H | 8.22997 | -0.59071 | -0.37959 | C | 0.92394 | -0.89830 | -1.77524 |
| H | 7.48843 | 0.77366 | -1.26819 | C | -1.07442 | -1.20807 | -0.40584 |
| H | 7.28069 | -0.87107 | -1.87021 | C | 1.14152 | -1.77751 | 0.43375 |
| C | 0.80656 | 2.52130 | -0.02193 | C | 1.75802 | -1.30684 | -0.73127 |
| H | 2.85140 | 2.64068 | 0.65160 | C | -0.45907 | -0.86491 | -1.61659 |
| H | 1.98223 | 1.24631 | 1.22851 | C | -2.57319 | -1.04713 | -0.21830 |
| C | -0.20391 | 1.79468 | -0.53795 | H | 1.76273 | -2.17009 | 1.23843 |
| C | 0.72981 | 3.99280 | 0.31196 | C | 3.25782 | -1.15948 | -0.84332 |
| H | -0.25033 | 4.43346 | 0.11774 | H | -1.06756 | -0.53635 | -2.45147 |
| H | 1.47307 | 4.55626 | -0.26953 | H | 1.36116 | -0.58147 | -2.71971 |
| H | 0.97125 | 4.16584 | 1.36986 | H | -0.02545 | -2.87806 | 2.41776 |
| C | -2.79951 | 1.55043 | -0.24336 | H | -1.65079 | -2.94881 | 1.74055 |
| H | -0.00184 | 0.74617 | -0.74117 | O | -1.30873 | -1.28049 | 2.81203 |
| H | -3.66949 | 2.15109 | -0.54011 | H | -0.57165 | -0.68888 | 3.03046 |
| H | -2.69707 | 1.65555 | 0.84112 | H | -2.80495 | -1.40492 | 0.78583 |
| C | -3.18003 | 0.07888 | -0.58180 | C | -3.41867 | -1.89095 | -1.21546 |
| C | -2.91394 | -0.19079 | -2.07649 | C | 3.81605 | 0.07158 | -0.08332 |
| C | -4.73292 | -0.15219 | -0.30578 | H | 3.53273 | -1.03602 | -1.89778 |
| H | -3.41922 | 0.56261 | -2.69159 | H | 3.77884 | -2.04806 | -0.47009 |
| H | -3.26411 | -1.17859 | -2.39947 | C | 3.01991 | 1.37454 | -0.28677 |
| H | -1.84986 | -0.13448 | -2.31560 | O | 5.17342 | 0.30746 | -0.56088 |
| O | -5.56660 | 0.47214 | -1.28433 | H | 3.89306 | -0.16354 | 0.98184 |
| C | -5.23141 | 0.44095 | 1.01988 | H | 2.43727 | 1.30963 | -1.21185 |
| H | -3.10253 | -2.94157 | -0.59520 | H | 3.73670 | 2.19050 | -0.42327 |

| | | | |
|---|---|---|---|
| C | 2.08247 | 1.67934 | 0.91603 |
| C | 6.16582 | -0.40773 | 0.01871 |
| O | 5.99323 | -1.22817 | 0.89489 |
| C | 7.50575 | -0.03777 | -0.57572 |
| H | 8.29295 | -0.60518 | -0.07820 |
| H | 7.68767 | 1.03561 | -0.46023 |
| H | 7.51278 | -0.25567 | -1.64892 |
| C | 0.77087 | 2.36755 | 0.58311 |
| H | 2.64697 | 2.29476 | 1.63456 |
| H | 1.85176 | 0.74475 | 1.43647 |
| C | -0.38347 | 1.82380 | 1.00297 |
| C | 0.87558 | 3.67717 | -0.15962 |
| H | -0.09971 | 4.11768 | -0.38137 |
| H | 1.41392 | 3.55936 | -1.10937 |
| H | 1.44464 | 4.41094 | 0.42975 |
| C | -2.92938 | 1.31598 | 0.93628 |
| H | -0.31668 | 0.89003 | 1.55668 |
| H | -3.83920 | 1.90955 | 1.11159 |
| H | -2.79375 | 0.70132 | 1.83400 |
| C | -3.22796 | 0.39030 | -0.28125 |
| C | -2.93033 | 1.14234 | -1.59167 |
| C | -4.76399 | -0.03213 | -0.28837 |
| H | -3.52759 | 2.05714 | -1.64215 |
| H | -3.18510 | 0.55348 | -2.47836 |
| H | -1.87483 | 1.41565 | -1.65890 |
| O | -5.61228 | 0.99113 | -0.82138 |
| C | -5.31815 | -0.43739 | 1.08975 |
| H | -2.95488 | -1.89664 | -2.20704 |
| C | -4.81520 | -1.22755 | -1.26523 |
| H | -3.46021 | -2.93679 | -0.89139 |
| H | -5.62131 | -1.91858 | -0.99808 |
| H | -5.04453 | -0.84766 | -2.26511 |
| H | -5.71289 | 1.67614 | -0.14062 |
| H | -5.30018 | 0.39575 | 1.80197 |
| H | -4.76879 | -1.26694 | 1.54517 |
| H | -6.36051 | -0.74906 | 0.96514 |
| C | -1.78694 | 2.36264 | 0.87701 |
| H | -1.89378 | 2.98937 | -0.01465 |
| H | -1.96673 | 3.04096 | 1.72733 |

---

Compound **5.5**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -227.082794 kJ.

| | | | |
|---|---|---|---|
| C | 18.79620 | -3.67920 | -9.09340 |
| C | 19.56620 | -2.37650 | -9.36910 |
| C | 19.28980 | -4.82440 | -9.96610 |
| H | 20.55600 | -2.46370 | -8.92060 |
| H | 19.74810 | -2.27890 | -10.44140 |
| C | 18.51870 | -5.67180 | -10.67760 |
| C | 19.11610 | -6.74570 | -11.56410 |
| C | 17.00130 | -5.62310 | -10.65260 |
| H | 20.20600 | -6.71440 | -11.55390 |
| H | 18.80270 | -7.73370 | -11.22620 |
| H | 18.78360 | -6.61190 | -12.59380 |
| H | 16.72270 | -5.42840 | -9.62070 |
| H | 16.58160 | -6.59960 | -10.89560 |
| C | 16.44230 | -4.53430 | -11.58450 |
| H | 17.05230 | -3.64420 | -11.45130 |
| C | 14.94790 | -4.18300 | -11.36780 |
| H | 16.60530 | -4.84720 | -12.61550 |
| C | 14.42510 | -3.04960 | -12.30250 |
| O | 14.75110 | -3.75280 | -10.02600 |
| H | 14.34680 | -5.07440 | -11.55980 |
| C | 15.12580 | -1.67420 | -12.09000 |
| H | 13.36930 | -2.92020 | -12.06100 |
| C | 14.47320 | -3.49100 | -13.78320 |
| H | 14.20000 | -4.54450 | -13.85590 |
| H | 15.49430 | -3.41940 | -14.16050 |
| C | 13.52860 | -2.70180 | -14.70390 |
| H | 13.78780 | -1.64450 | -14.75000 |
| H | 12.49420 | -2.77820 | -14.36800 |
| H | 13.57240 | -3.08960 | -15.72200 |
| H | 15.07250 | -1.07640 | -12.99840 |
| H | 16.19270 | -1.80640 | -11.93960 |
| C | 14.53310 | -0.81440 | -10.95530 |
| C | 15.51840 | 0.18780 | -10.32560 |
| H | 14.13390 | -1.44070 | -10.16930 |
| H | 13.67260 | -0.27230 | -11.34860 |
| H | 15.94840 | 0.82830 | -11.09840 |
| N | 16.56020 | -0.46290 | -9.52840 |
| H | 16.32680 | -0.75930 | -8.58330 |
| C | 17.84370 | -0.57540 | -9.89450 |
| O | 18.24430 | -0.23410 | -11.00700 |
| C | 18.84330 | -1.10870 | -8.84810 |
| C | 19.86480 | -0.01210 | -8.46270 |
| H | 18.30230 | -1.37870 | -7.94060 |
| C | 19.25490 | 1.19150 | -7.72380 |
| H | 20.38650 | 0.33650 | -9.35580 |
| H | 20.63090 | -0.44540 | -7.81940 |
| H | 18.54840 | 1.73400 | -8.35290 |
| H | 20.03160 | 1.89550 | -7.42460 |

| | | | |
|---|---|---|---|
| H | 18.72740 | 0.87540 | -6.82320 |
| H | 20.36380 | -4.93340 | -10.01310 |
| H | 18.91070 | -3.96160 | -8.04630 |
| H | 17.73200 | -3.50510 | -9.24320 |
| H | 14.97340 | 0.85430 | -9.65690 |
| C | 14.50610 | -4.18200 | -7.71080 |
| C | 14.16790 | -4.66350 | -9.14580 |
| C | 12.00790 | -3.59000 | -9.09140 |
| C | 12.20690 | -3.09570 | -7.64160 |
| C | 13.71800 | -2.89380 | -7.42010 |
| H | 14.58170 | -5.65690 | -9.31870 |
| H | 15.57280 | -3.94940 | -7.68890 |
| H | 12.35000 | -2.81700 | -9.77920 |
| H | 11.69150 | -2.14010 | -7.52990 |
| H | 14.02790 | -2.15900 | -8.15990 |
| O | 12.77860 | -4.77000 | -9.31880 |
| O | 14.23890 | -5.19240 | -6.74270 |
| O | 11.61530 | -4.05130 | -6.76040 |
| C | 10.54500 | -3.89180 | -9.44180 |
| H | 9.91270 | -3.01930 | -9.27770 |
| H | 10.45170 | -4.17960 | -10.48900 |
| H | 10.15120 | -4.71130 | -8.84020 |
| C | 11.22470 | -3.71320 | -5.52920 |
| C | 10.56430 | -4.86490 | -4.79070 |
| H | 10.27240 | -4.55550 | -3.78730 |
| H | 11.25450 | -5.70440 | -4.71020 |
| H | 9.67440 | -5.19440 | -5.32620 |
| O | 11.39140 | -2.61600 | -4.99860 |
| C | 15.10870 | -6.18730 | -6.55340 |
| O | 16.15470 | -6.35740 | -7.17490 |
| C | 14.66570 | -7.14600 | -5.46100 |
| H | 14.62000 | -6.62930 | -4.50290 |
| H | 13.67980 | -7.54900 | -5.69060 |
| H | 15.36960 | -7.97380 | -5.37700 |
| N | 14.04510 | -2.30770 | -6.12160 |
| H | 13.37240 | -2.44890 | -5.37690 |
| C | 15.12260 | -1.55180 | -5.89460 |
| O | 15.93720 | -1.27860 | -6.77440 |
| C | 15.30410 | -1.01620 | -4.48310 |
| H | 16.17480 | -0.36150 | -4.43360 |
| H | 14.42920 | -0.44430 | -4.17390 |
| H | 15.45400 | -1.83640 | -3.78120 |

---

Compound **5.5**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -225.507904 kJ.

| | | | |
|---|---|---|---|
| C | 19.85930 | -2.83580 | -11.12960 |
| C | 20.32330 | -1.74940 | -10.13740 |
| C | 19.69560 | -4.19550 | -10.46890 |
| H | 21.14030 | -2.14900 | -9.53640 |
| H | 20.76920 | -0.93060 | -10.70500 |
| C | 18.65180 | -5.04560 | -10.55480 |
| C | 18.67810 | -6.37540 | -9.82270 |
| C | 17.38590 | -4.78900 | -11.36270 |
| H | 19.62960 | -6.53870 | -9.31620 |
| H | 17.89340 | -6.42130 | -9.06860 |
| H | 18.52800 | -7.19800 | -10.52220 |
| H | 17.12470 | -5.70260 | -11.89750 |
| H | 17.58210 | -4.04890 | -12.13170 |
| C | 16.21330 | -4.34870 | -10.47040 |
| H | 16.14350 | -5.08240 | -9.67250 |
| C | 14.82600 | -4.24650 | -11.16090 |
| H | 16.46270 | -3.40880 | -9.97760 |
| C | 14.70430 | -3.19990 | -12.31530 |
| O | 13.82180 | -3.89250 | -10.20800 |
| H | 14.55620 | -5.22790 | -11.55440 |
| C | 15.43680 | -1.85610 | -12.04770 |
| H | 13.64040 | -2.97190 | -12.40020 |
| C | 15.09200 | -3.80560 | -13.68700 |
| H | 14.71960 | -4.82860 | -13.75130 |
| H | 16.17340 | -3.87610 | -13.78880 |
| C | 14.52930 | -3.04000 | -14.89540 |
| H | 14.94340 | -2.03500 | -14.97450 |
| H | 13.44340 | -2.95340 | -14.84070 |
| H | 14.77010 | -3.55950 | -15.82340 |
| H | 15.42930 | -1.23900 | -12.94450 |
| H | 16.49210 | -2.04390 | -11.86040 |
| C | 14.83450 | -1.00460 | -10.91300 |
| C | 15.77450 | 0.09320 | -10.39520 |
| H | 14.58090 | -1.63200 | -10.06730 |
| H | 13.89790 | -0.56230 | -11.25350 |
| H | 16.09540 | 0.73580 | -11.21730 |
| N | 16.90150 | -0.50320 | -9.68600 |
| H | 16.68490 | -1.07230 | -8.87100 |
| C | 18.18930 | -0.35480 | -10.01520 |
| O | 18.55740 | 0.38280 | -10.92840 |
| C | 19.21780 | -1.17460 | -9.21260 |
| C | 19.85040 | -0.31190 | -8.09500 |
| H | 18.70470 | -2.01700 | -8.74560 |
| C | 18.89390 | 0.04190 | -6.94400 |

| | | | |
|---|---|---|---|
| H | 20.25450 | 0.60620 | -8.52550 |
| H | 20.70370 | -0.84070 | -7.66970 |
| H | 19.41060 | 0.61320 | -6.17260 |
| H | 18.49390 | -0.85860 | -6.47740 |
| H | 18.05170 | 0.64360 | -7.28680 |
| H | 20.54530 | -4.49870 | -9.87400 |
| H | 18.96250 | -2.51060 | -11.65200 |
| H | 20.62380 | -2.95240 | -11.89830 |
| H | 15.24190 | 0.73430 | -9.69240 |
| C | 14.09400 | -4.28700 | -7.85960 |
| C | 13.51210 | -4.81220 | -9.20130 |
| C | 11.37860 | -3.79120 | -8.77290 |
| C | 11.83900 | -3.19310 | -7.42250 |
| C | 13.36530 | -2.98120 | -7.49100 |
| H | 13.91190 | -5.79650 | -9.45240 |
| H | 15.15170 | -4.07230 | -8.00640 |
| H | 11.56050 | -3.05630 | -9.55920 |
| H | 11.34580 | -2.22830 | -7.29160 |
| H | 13.52290 | -2.27290 | -8.30180 |
| O | 12.12450 | -4.97320 | -9.07580 |
| O | 13.96690 | -5.25230 | -6.81880 |
| O | 11.42180 | -4.06930 | -6.37460 |
| C | 9.88400 | -4.13720 | -8.81270 |
| H | 9.27170 | -3.26570 | -8.58190 |
| H | 9.59800 | -4.49370 | -9.80220 |
| H | 9.63640 | -4.92210 | -8.09750 |
| C | 11.25350 | -3.62610 | -5.12630 |
| C | 10.74340 | -4.70600 | -4.18770 |
| H | 10.57750 | -4.29620 | -3.19150 |
| H | 11.46990 | -5.51500 | -4.11640 |
| H | 9.80290 | -5.11300 | -4.55810 |
| O | 11.50420 | -2.48880 | -4.72870 |
| C | 14.78560 | -6.30370 | -6.76550 |
| O | 15.66820 | -6.57160 | -7.57680 |
| C | 14.50930 | -7.19420 | -5.56600 |
| H | 13.50010 | -7.60070 | -5.62450 |
| H | 15.21760 | -8.02180 | -5.53900 |
| H | 14.60560 | -6.62360 | -4.64300 |
| N | 13.92420 | -2.33620 | -6.30380 |
| H | 13.32990 | -2.30950 | -5.48240 |
| C | 15.12430 | -1.74940 | -6.26450 |
| O | 15.87900 | -1.71220 | -7.23570 |
| C | 15.53360 | -1.10930 | -4.94710 |
| H | 14.72260 | -0.50090 | -4.54280 |
| H | 15.79240 | -1.87940 | -4.21850 |
| H | 16.40360 | -0.46520 | -5.08930 |

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Compound **5.5**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
SMD implicit solvation in ethanol was used.

Electronic Energy: -1884.71968063 hartree.
Free Energy: -1884.012002 hartree.

| | | | |
|---|---|---|---|
| C | -4.30398 | -2.09291 | -0.83465 |
| C | -5.42239 | -2.08127 | 0.22770 |
| C | -3.14334 | -2.97555 | -0.45393 |
| H | -5.87475 | -3.07978 | 0.28681 |
| H | -4.99695 | -1.87082 | 1.21721 |
| C | -1.84697 | -2.63083 | -0.35559 |
| C | -0.80354 | -3.64093 | 0.06281 |
| C | -1.32506 | -1.23372 | -0.64321 |
| H | -0.03268 | -3.75822 | -0.71264 |
| H | -0.27374 | -3.32052 | 0.97082 |
| H | -1.24267 | -4.62532 | 0.26022 |
| H | -1.98400 | -0.72428 | -1.35195 |
| H | -0.34696 | -1.31294 | -1.13489 |
| C | -1.17582 | -0.37079 | 0.62808 |
| H | -2.13883 | -0.30849 | 1.14714 |
| C | -0.64453 | 1.05463 | 0.38752 |
| H | -0.49213 | -0.86550 | 1.32912 |
| C | -1.47149 | 1.92901 | -0.58152 |
| O | 0.70364 | 0.97357 | -0.14896 |
| H | -0.58969 | 1.56239 | 1.36006 |
| C | -2.94161 | 2.01331 | -0.11149 |
| H | -1.47062 | 1.42376 | -1.55812 |
| C | -0.82508 | 3.31688 | -0.81247 |
| H | -1.44112 | 3.86152 | -1.53895 |
| H | 0.14638 | 3.17169 | -1.29823 |
| C | -0.62869 | 4.19156 | 0.43191 |
| H | 0.10658 | 3.76047 | 1.12130 |
| H | -1.56220 | 4.34107 | 0.98747 |
| H | -0.25854 | 5.18336 | 0.14350 |
| H | -2.99604 | 2.50130 | 0.87159 |
| H | -3.31721 | 0.99738 | 0.03664 |
| C | -3.89254 | 2.72562 | -1.08400 |
| C | -5.37603 | 2.56974 | -0.70948 |
| H | -3.74271 | 2.34078 | -2.10329 |
| H | -3.67885 | 3.80128 | -1.12279 |
| H | -5.54988 | 2.90569 | 0.31632 |
| N | -5.87487 | 1.19839 | -0.80673 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -6.08254 | 0.84061 | -1.73090 | O | 2.31536 | -2.45105 | -2.11368 |
| C | -6.01676 | 0.36049 | 0.24674 | C | 4.48494 | -3.43044 | -2.47903 |
| O | -5.74655 | 0.70044 | 1.41070 | H | 4.30029 | -4.35522 | -1.92051 |
| C | -6.53728 | -1.04844 | -0.05986 | H | 4.26296 | -3.63262 | -3.53199 |
| C | -7.79631 | -1.33231 | 0.78540 | H | 5.53979 | -3.16058 | -2.37847 |
| H | -6.81096 | -1.11169 | -1.12215 | ---------- | | | |
| C | -8.97113 | -0.39319 | 0.49774 | | | | |
| H | -7.52633 | -1.27199 | 1.84749 | Compound **5.5** | | | |
| H | -8.10219 | -2.36911 | 0.59597 | This structure was assigned as ambiguous. | | | |
| H | -9.84782 | -0.67234 | 1.09455 | B3LYP/6-31g(d) | | | |
| H | -9.26361 | -0.42985 | -0.55956 | Gas phase. | | | |
| H | -8.72698 | 0.64811 | 0.74100 | | | | |
| H | -3.41152 | -4.00984 | -0.22478 | Electronic Energy: -1884.66885819 har- | | | |
| H | -4.74140 | -2.44654 | -1.78216 | tree. | | | |
| H | -3.96623 | -1.06830 | -1.01738 | Free Energy: -1883.960471 hartree. | | | |
| H | -5.98867 | 3.19161 | -1.37127 | | | | |
| C | 2.55694 | -0.43411 | 0.38045 | C | -4.24809 | -2.10684 | -0.81982 |
| C | 1.74585 | 0.81199 | 0.78327 | C | -5.33561 | -2.07467 | 0.27418 |
| C | 3.26080 | 2.28670 | -0.38146 | C | -3.06726 | -2.96784 | -0.45233 |
| C | 4.18408 | 1.12976 | -0.79158 | H | -5.76384 | -3.07999 | 0.38530 |
| C | 3.34958 | -0.15539 | -0.90408 | H | -4.88790 | -1.81447 | 1.24054 |
| H | 1.35495 | 0.69173 | 1.79720 | C | -1.77794 | -2.60071 | -0.36656 |
| H | 1.87653 | -1.26898 | 0.22267 | C | -0.70873 | -3.58839 | 0.03927 |
| H | 2.52855 | 2.40622 | -1.18908 | C | -1.28281 | -1.19544 | -0.65853 |
| H | 4.65748 | 1.35324 | -1.75121 | H | 0.05134 | -3.68245 | -0.74798 |
| H | 2.58951 | 0.05304 | -1.66645 | H | -0.17735 | -3.25533 | 0.94154 |
| O | 2.56616 | 1.96733 | 0.84311 | H | -1.12835 | -4.57964 | 0.24198 |
| O | 3.48407 | -0.78471 | 1.43457 | H | -1.95661 | -0.69783 | -1.36267 |
| O | 5.22011 | 1.04801 | 0.22797 | H | -0.30807 | -1.25580 | -1.15781 |
| C | 3.98337 | 3.60396 | -0.15561 | C | -1.14652 | -0.33589 | 0.61729 |
| H | 4.51407 | 3.90410 | -1.06580 | H | -2.11140 | -0.28675 | 1.13495 |
| H | 3.25885 | 4.38596 | 0.09290 | C | -0.62661 | 1.09537 | 0.38386 |
| H | 4.70642 | 3.52558 | 0.66169 | H | -0.46279 | -0.83008 | 1.31893 |
| C | 6.44586 | 0.60116 | -0.09652 | C | -1.44760 | 1.96017 | -0.59801 |
| C | 7.40658 | 0.76806 | 1.04614 | O | 0.72533 | 1.03972 | -0.13191 |
| H | 7.01412 | 0.26678 | 1.93735 | H | -0.59612 | 1.60729 | 1.35745 |
| H | 8.37688 | 0.34752 | 0.77840 | C | -2.92143 | 2.05072 | -0.14387 |
| H | 7.51576 | 1.83143 | 1.28645 | H | -1.43425 | 1.44344 | -1.56832 |
| O | 6.72245 | 0.11692 | -1.18390 | C | -0.79755 | 3.34522 | -0.83808 |
| C | 3.04482 | -1.60720 | 2.41285 | H | -1.41837 | 3.89422 | -1.55763 |
| O | 1.90613 | -2.03675 | 2.47576 | H | 0.16727 | 3.18933 | -1.33180 |
| C | 4.14352 | -1.91553 | 3.39163 | C | -0.57987 | 4.21563 | 0.40703 |
| H | 4.54831 | -0.98590 | 3.80585 | H | 0.16864 | 3.77822 | 1.07640 |
| H | 3.75685 | -2.54300 | 4.19601 | H | -1.50360 | 4.36099 | 0.97923 |
| H | 4.96207 | -2.43410 | 2.87994 | H | -0.21664 | 5.20902 | 0.11822 |
| N | 4.12641 | -1.29954 | -1.35908 | H | -2.99394 | 2.58171 | 0.81494 |
| H | 5.13727 | -1.21549 | -1.36441 | H | -3.29617 | 1.04409 | 0.05516 |
| C | 3.54495 | -2.35642 | -1.97654 | C | -3.86819 | 2.70850 | -1.15842 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -5.35462 | 2.52900 | -0.80141 | H | 3.60925 | -2.53857 | 4.21798 |
| H | -3.68809 | 2.29112 | -2.16067 | H | 4.80824 | -2.53762 | 2.89025 |
| H | -3.67200 | 3.78605 | -1.23506 | N | 4.04360 | -1.28833 | -1.40838 |
| H | -5.54292 | 2.86849 | 0.22065 | H | 5.04969 | -1.19673 | -1.49508 |
| N | -5.82266 | 1.14773 | -0.86749 | C | 3.38860 | -2.32882 | -1.99967 |
| H | -6.02276 | 0.75109 | -1.77464 | O | 2.16161 | -2.39297 | -2.05194 |
| C | -5.97706 | 0.35471 | 0.23695 | C | 4.27595 | -3.41917 | -2.57927 |
| O | -5.72427 | 0.75305 | 1.37122 | H | 4.06406 | -4.35991 | -2.06100 |
| C | -6.47939 | -1.07447 | -0.01569 | H | 4.01482 | -3.56262 | -3.63215 |
| C | -7.70739 | -1.34781 | 0.87545 | H | 5.34534 | -3.20214 | -2.49987 |
| H | -6.78187 | -1.18098 | -1.06946 | --- | | | |
| C | -8.91385 | -0.45461 | 0.56900 | | | | |
| H | -7.40455 | -1.21196 | 1.92006 | Compound **5.5** | | | |
| H | -7.98994 | -2.40184 | 0.75545 | This structure was assigned as ambiguous. | | | |
| H | -9.76397 | -0.71292 | 1.21038 | M06-2X/6-31g(d) | | | |
| H | -9.24006 | -0.56399 | -0.47334 | SMD implicit solvation in ethanol was used. | | | |
| H | -8.68042 | 0.60208 | 0.74072 | | | | |
| H | -3.31473 | -4.00579 | -0.21939 | | | | |
| H | -4.70873 | -2.48679 | -1.74686 | Electronic Energy: -1883.93135469 hartree. | | | |
| H | -3.92611 | -1.08358 | -1.03835 | | | | |
| H | -5.97353 | 3.13217 | -1.47700 | Free Energy: -1883.211379 hartree. | | | |
| C | 2.53122 | -0.42318 | 0.38598 | | | | |
| C | 1.75352 | 0.83874 | 0.80660 | C | 2.51017 | 0.72121 | 2.16509 |
| C | 3.28601 | 2.29420 | -0.32690 | C | 1.54896 | 1.74822 | 1.55151 |
| C | 4.17834 | 1.12241 | -0.77522 | C | 1.76729 | -0.32255 | 2.95042 |
| C | 3.30952 | -0.13895 | -0.90458 | H | 0.85566 | 1.22168 | 0.88485 |
| H | 1.35204 | 0.71261 | 1.81574 | H | 0.94220 | 2.20340 | 2.34576 |
| H | 1.82698 | -1.23524 | 0.21345 | C | 1.76002 | -1.65282 | 2.78482 |
| H | 2.54932 | 2.45182 | -1.12637 | C | 0.96927 | -2.52119 | 3.73508 |
| H | 4.64726 | 1.34835 | -1.73893 | C | 2.57403 | -2.40740 | 1.75312 |
| H | 2.53072 | 0.10666 | -1.63885 | H | 0.59680 | -1.94236 | 4.58460 |
| O | 2.59856 | 1.97087 | 0.88792 | H | 0.10408 | -2.98979 | 3.25223 |
| O | 3.45991 | -0.82451 | 1.41851 | H | 1.59537 | -3.33648 | 4.12118 |
| O | 5.23039 | 1.00941 | 0.22238 | H | 3.32548 | -2.98803 | 2.30738 |
| C | 4.04652 | 3.58777 | -0.07560 | H | 3.13281 | -1.72485 | 1.10638 |
| H | 4.58238 | 3.90210 | -0.97837 | C | 1.76816 | -3.40299 | 0.89868 |
| H | 3.34292 | 4.37716 | 0.20331 | H | 2.42122 | -4.21943 | 0.57373 |
| H | 4.76559 | 3.45899 | 0.73706 | C | 1.08806 | -2.83867 | -0.35070 |
| C | 6.41428 | 0.47073 | -0.11046 | H | 0.99865 | -3.87972 | 1.51658 |
| C | 7.40555 | 0.61416 | 1.01804 | C | 1.99130 | -2.43273 | -1.53674 |
| H | 6.99216 | 0.17374 | 1.93081 | O | 0.31173 | -1.67675 | -0.02959 |
| H | 8.33945 | 0.11945 | 0.75006 | H | 0.40631 | -3.61430 | -0.72748 |
| H | 7.59080 | 1.67381 | 1.22265 | C | 2.56427 | -0.99556 | -1.45692 |
| O | 6.65155 | -0.06411 | -1.17923 | H | 1.31472 | -2.44954 | -2.40499 |
| C | 2.95125 | -1.55477 | 2.43822 | C | 3.07639 | -3.47987 | -1.81253 |
| O | 1.77825 | -1.84192 | 2.55234 | H | 2.63483 | -4.48444 | -1.76165 |
| C | 4.04057 | -1.95178 | 3.40647 | H | 3.83795 | -3.43145 | -1.02255 |
| H | 4.52478 | -1.05689 | 3.81145 | C | 3.74232 | -3.29404 | -3.17329 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 4.23679 | -2.31929 | -3.25075 | H | -6.25062 | -0.10680 | -1.42744 |
| H | 3.00523 | -3.36149 | -3.98182 | O | -3.96641 | 1.88935 | -2.18925 |
| H | 4.50209 | -4.06284 | -3.34748 | C | -2.86862 | -0.87746 | 2.75669 |
| H | 3.66180 | -1.02254 | -1.40289 | O | -1.90943 | -1.08476 | 3.46483 |
| H | 2.22024 | -0.49185 | -0.54695 | C | -4.30244 | -0.90482 | 3.18990 |
| C | 2.13021 | -0.16140 | -2.66504 | H | -4.36283 | -1.19475 | 4.23833 |
| C | 2.65727 | 1.27113 | -2.66805 | H | -4.74559 | 0.08579 | 3.05059 |
| H | 1.03049 | -0.13046 | -2.69707 | H | -4.85951 | -1.61159 | 2.56870 |
| H | 2.45431 | -0.65133 | -3.59295 | N | -1.94442 | 1.75288 | 0.14709 |
| H | 3.75004 | 1.28266 | -2.64633 | H | -2.72691 | 1.78435 | 0.79176 |
| N | 2.19394 | 2.03370 | -1.52056 | C | -1.56454 | 2.88620 | -0.48054 |
| H | 1.20553 | 2.28108 | -1.47597 | O | -0.68666 | 2.89038 | -1.35033 |
| C | 2.95628 | 2.24534 | -0.43038 | C | -2.28669 | 4.14361 | -0.07739 |
| O | 4.14623 | 1.91207 | -0.36775 | H | -2.83547 | 4.03044 | 0.85973 |
| C | 2.22959 | 2.87677 | 0.75097 | H | -1.56504 | 4.95866 | 0.01047 |
| C | 3.17570 | 3.73086 | 1.59347 | H | -2.99349 | 4.39822 | -0.87421 |
| H | 1.43258 | 3.52018 | 0.35335 | ---------- | | | |
| C | 3.66830 | 4.96699 | 0.84622 | | | | |
| H | 4.03418 | 3.12570 | 1.90282 | Compound **5.5** | | | |
| H | 2.64852 | 4.03155 | 2.50755 | This structure was assigned as correct. | | | |
| H | 4.32387 | 5.57676 | 1.47599 | B3LYP/6-31g(d) | | | |
| H | 2.82859 | 5.59582 | 0.52905 | Gas phase. | | | |
| H | 4.23422 | 4.68442 | -0.04834 | | | | |
| H | 1.16314 | 0.07791 | 3.76883 | Electronic Energy: -1884.66993152 hartree. | | | |
| H | 3.12385 | 0.27094 | 1.37877 | | | | |
| H | 3.20132 | 1.24153 | 2.84276 | Free Energy: -1883.962136 hartree. | | | |
| H | 2.33420 | 1.78564 | -3.57869 | | | | |
| C | -1.44010 | -0.50405 | 0.90042 | C | 2.75493 | 1.08287 | 2.04173 |
| C | -0.99149 | -1.88073 | 0.41351 | C | 3.84483 | 1.88338 | 1.29681 |
| C | -1.86038 | -1.53754 | -1.78087 | C | 3.34045 | 0.14078 | 3.06665 |
| C | -2.27703 | -0.10222 | -1.46343 | H | 4.24935 | 2.64728 | 1.97448 |
| C | -1.47125 | 0.45659 | -0.28038 | H | 4.67805 | 1.22360 | 1.03052 |
| H | -1.05129 | -2.62852 | 1.21463 | C | 2.98435 | -1.13402 | 3.28992 |
| H | -0.74942 | -0.14718 | 1.66802 | C | 3.69269 | -1.98524 | 4.31493 |
| H | -0.84234 | -1.48303 | -2.18735 | C | 1.85436 | -1.80473 | 2.52210 |
| H | -2.10867 | 0.52414 | -2.34389 | H | 4.51336 | -1.44480 | 4.79755 |
| H | -0.44106 | 0.57351 | -0.63272 | H | 3.00145 | -2.32517 | 5.09952 |
| O | -1.84608 | -2.35323 | -0.60338 | H | 4.11089 | -2.89317 | 3.85680 |
| O | -2.76271 | -0.58222 | 1.44467 | H | 1.01664 | -1.10564 | 2.44271 |
| O | -3.67508 | -0.08694 | -1.14033 | H | 1.48476 | -2.67155 | 3.08692 |
| C | -2.77908 | -2.21324 | -2.77741 | C | 2.26101 | -2.24581 | 1.09935 |
| H | -2.83489 | -1.62426 | -3.69795 | H | 2.85917 | -1.45057 | 0.64821 |
| H | -2.39492 | -3.20727 | -3.02226 | C | 1.07686 | -2.57119 | 0.17469 |
| H | -3.78554 | -2.31637 | -2.36330 | H | 2.91391 | -3.12547 | 1.15591 |
| C | -4.40928 | 0.96628 | -1.54090 | C | 1.48030 | -2.92692 | -1.27992 |
| C | -5.82606 | 0.83446 | -1.06777 | O | 0.17201 | -1.43412 | 0.16753 |
| H | -5.83658 | 0.80926 | 0.02648 | H | 0.52387 | -3.42970 | 0.58196 |
| H | -6.41605 | 1.67669 | -1.42746 | C | 2.23897 | -1.79632 | -2.02375 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 0.53275 | -3.11672 | -1.80686 | H | -4.31289 | -2.42470 | -1.40781 |
| C | 2.27930 | -4.25260 | -1.29488 | C | -5.09551 | 0.55384 | -1.29258 |
| H | 1.87571 | -4.93345 | -0.53145 | C | -6.39670 | 0.64855 | -0.53103 |
| H | 3.32135 | -4.05595 | -1.00941 | H | -7.17375 | 1.04087 | -1.18762 |
| C | 2.25041 | -4.97201 | -2.64847 | H | -6.68860 | -0.33937 | -0.15951 |
| H | 2.65840 | -4.34790 | -3.45155 | H | -6.27691 | 1.30509 | 0.33719 |
| H | 1.22513 | -5.24414 | -2.92769 | O | -4.93790 | 0.86885 | -2.44989 |
| H | 2.84302 | -5.89328 | -2.61577 | C | -3.46199 | 0.32032 | 2.67605 |
| H | 2.90242 | -2.24764 | -2.77246 | O | -3.21319 | 1.51186 | 2.71214 |
| H | 2.91146 | -1.27437 | -1.33790 | C | -4.56437 | -0.34587 | 3.46297 |
| C | 1.34829 | -0.76567 | -2.74185 | H | -4.14650 | -1.11172 | 4.12413 |
| C | 2.05367 | 0.57093 | -3.03134 | H | -5.09888 | 0.40179 | 4.04954 |
| H | 0.46307 | -0.55118 | -2.13750 | H | -5.25193 | -0.84943 | 2.77582 |
| H | 0.98677 | -1.18919 | -3.69041 | N | -2.06443 | 2.01941 | 0.19866 |
| H | 3.05856 | 0.40085 | -3.42867 | H | -2.65145 | 2.22061 | 1.00154 |
| N | 2.19070 | 1.41998 | -1.85149 | C | -1.28372 | 3.00630 | -0.32288 |
| H | 1.38053 | 1.96707 | -1.57311 | O | -0.38306 | 2.79409 | -1.13830 |
| C | 3.34674 | 1.52444 | -1.14400 | C | -1.61318 | 4.41423 | 0.13882 |
| O | 4.35501 | 0.86384 | -1.40404 | H | -2.36144 | 4.44682 | 0.93573 |
| C | 3.35387 | 2.55692 | -0.00237 | H | -0.69407 | 4.89640 | 0.48409 |
| C | 4.27914 | 3.73066 | -0.39737 | H | -1.98121 | 4.98847 | -0.71785 |
| H | 2.33731 | 2.95029 | 0.14396 | --- | | | |
| C | 3.83719 | 4.49562 | -1.64939 | | | | |
| H | 5.29085 | 3.33250 | -0.54391 | Compound **5.26** | | | |
| H | 4.32972 | 4.42291 | 0.45387 | This structure was assigned as incorrect. | | | |
| H | 4.49467 | 5.35321 | -1.83285 | | | | |
| H | 2.81281 | 4.87470 | -1.54494 | Molecular Mechanics (OPLS-2005), gas phase. | | | |
| H | 3.86566 | 3.85968 | -2.54072 | | | | |
| H | 4.15856 | 0.55389 | 3.66027 | Energy: -178.794052 kJ. | | | |
| H | 2.07374 | 1.79769 | 2.53293 | | | | |
| H | 2.14222 | 0.53548 | 1.31758 | C | -2.65420 | -2.57030 | 7.54950 |
| H | 1.48249 | 1.13315 | -3.77976 | C | -1.41460 | -2.56230 | 6.63500 |
| C | -1.60463 | -0.24460 | 1.18642 | C | -3.67310 | -3.64740 | 7.14400 |
| C | -1.09770 | -1.62754 | 0.73049 | H | -0.86240 | -3.48760 | 6.80070 |
| C | -2.36638 | -1.49351 | -1.32869 | H | -1.73040 | -2.59380 | 5.59020 |
| C | -2.77993 | -0.03438 | -1.04654 | C | -4.90210 | -3.65780 | 8.04360 |
| C | -1.79326 | 0.61956 | -0.06827 | C | -4.86070 | -4.74380 | 9.11580 |
| H | -1.05308 | -2.30503 | 1.59010 | C | -5.92000 | -2.77850 | 7.90610 |
| H | -0.89217 | 0.22941 | 1.86688 | H | -3.94130 | -4.61680 | 9.68880 |
| H | -1.47170 | -1.42703 | -1.96148 | H | -4.78110 | -5.71040 | 8.61680 |
| H | -2.77662 | 0.51370 | -1.99133 | C | -6.05130 | -4.78340 | 10.08660 |
| H | -0.81681 | 0.60132 | -0.56297 | C | -6.00310 | -1.63820 | 6.90170 |
| O | -2.03025 | -2.23045 | -0.14027 | H | -5.14460 | -1.65090 | 6.23720 |
| O | -2.80527 | -0.58256 | 1.93272 | C | -6.13670 | -0.26050 | 7.58940 |
| O | -4.11402 | 0.05785 | -0.49077 | H | -6.86840 | -1.81730 | 6.26370 |
| C | -3.43552 | -2.30119 | -2.04915 | C | -5.95740 | 0.96080 | 6.64610 |
| H | -3.74015 | -1.79760 | -2.97179 | O | -5.19020 | -0.18180 | 8.64060 |
| H | -3.04784 | -3.29352 | -2.29671 | H | -7.13610 | -0.20820 | 8.02440 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Si | -5.52070 | 0.32230 | 10.21940 | C | -4.15090 | 0.49200 | 12.68460 |
| C | -4.49440 | 1.13840 | 6.15680 | C | -2.73850 | 0.46700 | 10.59630 |
| H | -6.21650 | 1.84330 | 7.23190 | C | -3.86810 | -1.63750 | 11.37200 |
| C | -6.96420 | 0.91430 | 5.47610 | H | -1.83530 | 0.23860 | 11.16250 |
| H | -7.93250 | 0.57620 | 5.84740 | H | -2.80080 | 1.55090 | 10.49410 |
| H | -6.64760 | 0.17220 | 4.74180 | H | -2.61730 | 0.04850 | 9.59660 |
| C | -7.17520 | 2.26950 | 4.78260 | H | -5.04640 | 0.11420 | 13.17940 |
| H | -6.25950 | 2.64160 | 4.32400 | H | -4.23050 | 1.57900 | 12.64850 |
| H | -7.52540 | 3.02390 | 5.48760 | H | -3.29830 | 0.24770 | 13.31890 |
| H | -7.92230 | 2.18550 | 3.99300 | H | -4.72440 | -2.07730 | 11.88370 |
| H | -4.47140 | 1.51130 | 5.13380 | H | -2.97220 | -1.93570 | 11.91670 |
| H | -3.99720 | 0.17300 | 6.10450 | H | -3.81820 | -2.08820 | 10.38050 |
| C | -3.66210 | 2.10010 | 7.02620 | | | | |
| C | -2.16610 | 2.11950 | 6.67140 | ---------- | | | |
| H | -3.76720 | 1.83960 | 8.07680 | | | | |
| H | -4.06820 | 3.10700 | 6.92390 | Compound **5.26** | | | |
| H | -2.02920 | 2.33360 | 5.60930 | This structure was assigned as ambiguous. | | | |
| N | -1.51490 | 0.87210 | 7.06020 | | | | |
| H | -1.67500 | 2.93090 | 7.20890 | Molecular Mechanics (OPLS-2005), gas | | | |
| H | -1.40970 | 0.69270 | 8.04580 | phase. | | | |
| C | -1.10110 | -0.08260 | 6.21870 | Energy: -176.385025 kJ. | | | |
| O | -1.20240 | 0.01700 | 4.99750 | | | | |
| C | -0.48320 | -1.34570 | 6.84720 | C | -2.56880 | -3.36890 | 6.83540 |
| C | 0.92480 | -1.62550 | 6.26930 | C | -1.06010 | -3.05400 | 6.92180 |
| H | -0.37060 | -1.19190 | 7.92130 | C | -3.35450 | -2.95880 | 8.09250 |
| C | 1.98030 | -0.56300 | 6.61950 | H | -0.63950 | -3.63380 | 7.74390 |
| H | 0.86380 | -1.72910 | 5.18430 | H | -0.57310 | -3.43140 | 6.02080 |
| H | 1.28020 | -2.58770 | 6.63870 | C | -4.81940 | -3.36610 | 8.04040 |
| H | 2.95630 | -0.84490 | 6.22340 | C | -5.10000 | -4.73610 | 8.65160 |
| H | 2.08260 | -0.44550 | 7.69850 | C | -5.77680 | -2.56610 | 7.52260 |
| H | 1.72760 | 0.40980 | 6.19620 | H | -4.73990 | -4.73050 | 9.68110 |
| H | -3.14190 | -1.59590 | 7.52910 | H | -4.49880 | -5.47450 | 8.11980 |
| H | -2.34160 | -2.72740 | 8.58210 | C | -6.56970 | -5.18640 | 8.64560 |
| H | -3.20190 | -4.63080 | 7.16200 | C | -5.55710 | -1.21790 | 6.85850 |
| H | -3.98280 | -3.50080 | 6.10920 | H | -4.52310 | -1.13160 | 6.53690 |
| H | -6.76520 | -2.82840 | 8.57380 | C | -5.93500 | -0.03340 | 7.76470 |
| H | -5.93110 | -5.59430 | 10.80540 | H | -6.15820 | -1.21040 | 5.94990 |
| H | -6.99200 | -4.95150 | 9.56150 | C | -5.95380 | 1.36300 | 7.08360 |
| H | -6.13230 | -3.85750 | 10.65460 | O | -4.99890 | 0.01220 | 8.82730 |
| C | -5.82850 | 2.18340 | 10.22180 | H | -6.92920 | -0.22310 | 8.17480 |
| C | -7.04860 | -0.57720 | 10.86360 | Si | -5.40090 | 0.06150 | 10.46710 |
| C | -3.99170 | -0.10770 | 11.27740 | C | -4.56190 | 1.84660 | 6.59850 |
| H | -7.94350 | -0.30160 | 10.30850 | H | -6.22750 | 2.04890 | 7.88660 |
| H | -7.22950 | -0.34560 | 11.91220 | C | -7.07390 | 1.50090 | 6.02840 |
| H | -6.93220 | -1.65580 | 10.78450 | H | -8.00110 | 1.10260 | 6.44230 |
| H | -4.95140 | 2.73480 | 9.88880 | H | -6.85700 | 0.89050 | 5.15200 |
| H | -6.07570 | 2.54100 | 11.22020 | C | -7.33300 | 2.94910 | 5.58730 |
| H | -6.65460 | 2.45130 | 9.56530 | H | -6.46510 | 3.37950 | 5.08830 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -7.58010 | 3.58440 | 6.43810 | H | -3.21930 | 0.64790 | 13.53830 |
| H | -8.16740 | 2.99630 | 4.88720 | H | -3.15960 | -1.68350 | 11.42440 |
| H | -3.83100 | 1.61460 | 7.37190 | H | -1.84840 | -0.54500 | 11.70650 |
| H | -4.56050 | 2.93620 | 6.55850 | H | -2.51960 | -0.72970 | 10.09350 |
| C | -4.08890 | 1.32430 | 5.22080 | | | | |
| C | -2.56580 | 1.14610 | 5.11210 | --- | | | |
| H | -4.56080 | 0.37910 | 4.96470 | | | | |
| H | -4.42410 | 2.01580 | 4.44700 | Compound **5.26** | | | |
| H | -2.31350 | 0.82290 | 4.09990 | This structure was assigned as ambiguous. | | | |
| N | -2.07880 | 0.18850 | 6.10110 | M06-2X/6-31g(d) | | | |
| H | -2.05910 | 2.09910 | 5.26830 | SMD implicit solvation in toluene was used. | | | |
| H | -2.50310 | 0.21630 | 7.01640 | | | | |
| C | -1.11370 | -0.71570 | 5.89560 | | | | |
| O | -0.56450 | -0.86780 | 4.80640 | Electronic Energy: -1476.38772573 hartree. | | | |
| C | -0.68380 | -1.56200 | 7.10770 | | | | |
| C | 0.83280 | -1.41850 | 7.37810 | Free Energy: -1475.740673 hartree. | | | |
| H | -1.19340 | -1.18650 | 7.99430 | | | | |
| C | 1.26760 | -0.01370 | 7.82950 | C | -1.95038 | -2.02093 | 0.69531 |
| H | 1.39560 | -1.70160 | 6.48660 | C | -3.42322 | -2.00222 | 1.10615 |
| H | 1.12840 | -2.12760 | 8.15180 | C | -1.70913 | -2.50110 | -0.74228 |
| H | 2.33540 | 0.00720 | 8.04890 | H | -3.85694 | -3.00167 | 0.96980 |
| H | 0.73840 | 0.29470 | 8.73160 | H | -3.49698 | -1.75853 | 2.17180 |
| H | 1.08030 | 0.73280 | 7.05690 | C | -0.23312 | -2.64866 | -1.05026 |
| H | -3.00000 | -2.89230 | 5.95420 | C | 0.29968 | -4.05542 | -0.88169 |
| H | -2.68770 | -4.44110 | 6.67510 | C | 0.54626 | -1.61384 | -1.38535 |
| H | -3.30030 | -1.88190 | 8.23350 | H | -0.33161 | -4.72779 | -1.47956 |
| H | -2.89470 | -3.38780 | 8.98350 | H | 0.13451 | -4.36308 | 0.16245 |
| H | -6.80910 | -2.87800 | 7.54450 | C | 1.75768 | -4.28535 | -1.25858 |
| H | -7.19860 | -4.50300 | 9.21740 | C | 0.09871 | -0.19536 | -1.59339 |
| H | -6.66910 | -6.17380 | 9.09700 | H | 0.35173 | 0.10579 | -2.62162 |
| H | -6.96360 | -5.25180 | 7.63080 | C | 0.74617 | 0.82931 | -0.64335 |
| C | -6.65510 | 1.44350 | 10.74060 | H | -0.98754 | -0.11626 | -1.48905 |
| C | -6.14190 | -1.59940 | 10.96100 | C | 0.55092 | 2.26950 | -1.15719 |
| C | -3.79820 | 0.41010 | 11.44420 | O | 2.13871 | 0.56334 | -0.54083 |
| H | -5.43210 | -2.40860 | 10.79630 | H | 0.27549 | 0.72682 | 0.34939 |
| H | -7.03290 | -1.82760 | 10.37860 | Si | 2.89371 | 0.08892 | 0.87681 |
| H | -6.41950 | -1.61630 | 12.01360 | C | -0.93332 | 2.62512 | -1.34204 |
| H | -6.25650 | 2.40570 | 10.42220 | H | 1.02653 | 2.29276 | -2.15043 |
| H | -6.92270 | 1.53320 | 11.79240 | C | 1.28107 | 3.29187 | -0.27816 |
| H | -7.57310 | 1.26810 | 10.18220 | H | 0.89922 | 3.23580 | 0.75093 |
| C | -4.11440 | 0.44650 | 12.94910 | H | 2.33804 | 3.01056 | -0.23379 |
| C | -3.22590 | 1.76560 | 10.99510 | C | 1.16910 | 4.72769 | -0.78691 |
| C | -2.77460 | -0.70010 | 11.15250 | H | 0.14416 | 5.10877 | -0.72618 |
| H | -3.91860 | 2.58140 | 11.20400 | H | 1.48938 | 4.79944 | -1.83303 |
| H | -3.02740 | 1.77390 | 9.92220 | H | 1.80238 | 5.39905 | -0.19860 |
| H | -2.28950 | 1.99240 | 11.50550 | H | -1.41815 | 1.85736 | -1.95623 |
| H | -4.52510 | -0.50360 | 13.29270 | H | -1.00636 | 3.55251 | -1.92378 |
| H | -4.84270 | 1.22310 | 13.18530 | C | -1.71764 | 2.80260 | -0.03758 |

| | | | |
|---|---|---|---|
| C | -3.22343 | 2.63352 | -0.24061 |
| H | -1.41023 | 2.07486 | 0.72297 |
| H | -1.52233 | 3.79474 | 0.38754 |
| H | -3.76582 | 2.99797 | 0.63638 |
| N | -3.58861 | 1.23648 | -0.43566 |
| H | -3.56322 | 3.19818 | -1.11482 |
| H | -3.84911 | 0.90457 | -1.35314 |
| C | -3.76754 | 0.41987 | 0.63669 |
| O | -3.55505 | 0.79943 | 1.78180 |
| C | -4.28086 | -0.98537 | 0.34572 |
| C | -5.75162 | -1.06672 | 0.78456 |
| H | -4.22761 | -1.17767 | -0.73488 |
| C | -6.66582 | -0.09126 | 0.04885 |
| H | -5.79529 | -0.87467 | 1.86333 |
| H | -6.10079 | -2.09415 | 0.62731 |
| H | -7.71025 | -0.23947 | 0.33942 |
| H | -6.60186 | -0.22875 | -1.03724 |
| H | -6.40634 | 0.94925 | 0.27226 |
| H | -1.39614 | -2.67386 | 1.38170 |
| H | -1.51857 | -1.01709 | 0.81730 |
| H | -2.20707 | -3.47078 | -0.87771 |
| H | -2.18360 | -1.81175 | -1.45007 |
| H | 1.60801 | -1.78583 | -1.55241 |
| H | 1.94325 | -4.01130 | -2.30229 |
| H | 2.02042 | -5.34028 | -1.13506 |
| H | 2.44090 | -3.69945 | -0.63589 |
| C | 2.82102 | 1.43617 | 2.18699 |
| C | 2.07259 | -1.42358 | 1.63539 |
| C | 4.67632 | -0.25665 | 0.34690 |
| H | 2.54687 | -1.66423 | 2.59501 |
| H | 2.12336 | -2.31158 | 0.99888 |
| H | 1.01245 | -1.23097 | 1.83992 |
| H | 3.34255 | 2.35471 | 1.90016 |
| H | 3.27206 | 1.07095 | 3.11792 |
| H | 1.78305 | 1.70043 | 2.42116 |
| C | 5.53995 | -0.55512 | 1.57871 |
| C | 5.23730 | 0.97007 | -0.38497 |
| C | 4.70618 | -1.46387 | -0.59941 |
| H | 5.24259 | 1.86177 | 0.25430 |
| H | 4.65230 | 1.20379 | -1.28095 |
| H | 6.27541 | 0.78647 | -0.69720 |
| H | 5.16453 | -1.41777 | 2.14357 |
| H | 5.58443 | 0.30108 | 2.26233 |
| H | 6.57112 | -0.78701 | 1.27684 |
| H | 4.37316 | -2.37959 | -0.09592 |
| H | 5.72890 | -1.64324 | -0.96094 |
| H | 4.06691 | -1.30473 | -1.47620 |

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Compound **5.26**

This structure was assigned as ambiguous.

B3LYP/6-31g(d)

SMD implicit solvation in toluene was used.

Electronic Energy: -1476.98214928 hartree.

Free Energy: -1476.341768 hartree.

| | | | |
|---|---|---|---|
| C | -2.35687 | 2.12781 | -0.75368 |
| C | -3.84974 | 1.77177 | -0.84946 |
| C | -1.88133 | 2.51372 | 0.66556 |
| H | -4.13764 | 1.73490 | -1.90660 |
| H | -4.44571 | 2.56953 | -0.38478 |
| C | -0.40138 | 2.84430 | 0.72285 |
| C | -0.01488 | 4.24366 | 0.27438 |
| C | 0.54766 | 1.98127 | 1.12913 |
| H | -0.53948 | 4.49341 | -0.65890 |
| H | 1.05727 | 4.27118 | 0.04433 |
| C | -0.32406 | 5.33181 | 1.31793 |
| C | 0.36007 | 0.58183 | 1.65318 |
| H | 0.99372 | 0.44855 | 2.53940 |
| C | 0.70039 | -0.54775 | 0.64940 |
| H | -0.67499 | 0.43210 | 1.98020 |
| C | 0.20872 | -1.93224 | 1.15156 |
| O | 2.11168 | -0.57603 | 0.41852 |
| H | 0.17693 | -0.31608 | -0.28735 |
| Si | 3.02255 | -0.28280 | -0.96225 |
| C | 0.15778 | -2.98598 | 0.02345 |
| H | -0.81654 | -1.76944 | 1.51561 |
| C | 1.04227 | -2.45174 | 2.34667 |
| H | 1.27871 | -1.61882 | 3.01915 |
| H | 2.00692 | -2.81847 | 1.97496 |
| C | 0.35443 | -3.54779 | 3.16965 |
| H | 0.14512 | -4.44804 | 2.58034 |
| H | -0.59872 | -3.19550 | 3.58600 |
| H | 0.98543 | -3.85443 | 4.01260 |
| H | -0.07174 | -3.96328 | 0.46880 |
| H | 1.16772 | -3.08234 | -0.39387 |
| C | -0.82952 | -2.76555 | -1.13811 |
| C | -2.32907 | -2.85332 | -0.79485 |
| H | -0.64937 | -1.81241 | -1.64964 |
| H | -0.62939 | -3.54655 | -1.88463 |
| H | -2.89021 | -3.05884 | -1.70995 |
| N | -2.91575 | -1.64184 | -0.22479 |
| H | -2.51053 | -3.68097 | -0.09788 |

| | | | |
|---|---|---|---|
| H | -2.91558 | -1.52665 | 0.77865 |
| C | -3.59414 | -0.72996 | -0.98215 |
| O | -3.69142 | -0.83104 | -2.20481 |
| C | -4.25617 | 0.42419 | -0.21676 |
| C | -5.79211 | 0.24770 | -0.25164 |
| H | -3.93478 | 0.39817 | 0.83405 |
| C | -6.30781 | -1.00398 | 0.46452 |
| H | -6.11133 | 0.23095 | -1.30109 |
| H | -6.24654 | 1.13804 | 0.20265 |
| H | -5.93487 | -1.92414 | -0.00003 |
| H | -7.40308 | -1.04328 | 0.43633 |
| H | -6.00640 | -1.01571 | 1.52037 |
| H | -1.75371 | 1.28996 | -1.12640 |
| H | -2.15664 | 2.96520 | -1.43440 |
| H | -2.46655 | 3.38266 | 0.99861 |
| H | -2.11959 | 1.70343 | 1.36271 |
| H | 1.58152 | 2.32485 | 1.09465 |
| H | -1.39033 | 5.36534 | 1.57069 |
| H | -0.04409 | 6.32272 | 0.94031 |
| H | 0.23295 | 5.15387 | 2.24520 |
| C | 3.19082 | -1.85472 | -2.00312 |
| C | 2.23107 | 1.03872 | -2.05683 |
| C | 4.74287 | 0.26491 | -0.31227 |
| H | 2.21132 | 2.02946 | -1.59101 |
| H | 2.78050 | 1.12477 | -3.00328 |
| H | 1.19612 | 0.78184 | -2.31504 |
| H | 3.57813 | -2.70269 | -1.42625 |
| H | 3.87201 | -1.69357 | -2.84912 |
| H | 2.22635 | -2.15774 | -2.42918 |
| C | 4.60294 | 1.49446 | 0.60849 |
| C | 5.65799 | 0.63294 | -1.49958 |
| C | 5.39391 | -0.88251 | 0.48896 |
| H | 5.25823 | 1.47136 | -2.08369 |
| H | 5.80952 | -0.20988 | -2.18565 |
| H | 6.65180 | 0.93606 | -1.13774 |
| H | 3.97165 | 1.27985 | 1.47803 |
| H | 4.17231 | 2.35604 | 0.08250 |
| H | 5.58865 | 1.80730 | 0.98490 |
| H | 4.77835 | -1.18146 | 1.34562 |
| H | 5.56196 | -1.77333 | -0.12896 |
| H | 6.37399 | -0.57040 | 0.88041 |

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Compound **5.26**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1476.96062108 hartree.
Free Energy: -1476.320359 hartree.

| | | | |
|---|---|---|---|
| C | 2.65926 | -1.37993 | -1.73359 |
| C | 3.84016 | -1.61032 | -0.77600 |
| C | 1.29217 | -1.86545 | -1.20504 |
| H | 3.93553 | -2.68555 | -0.56863 |
| H | 4.76189 | -1.29895 | -1.28127 |
| C | 0.17284 | -1.71997 | -2.22460 |
| C | -0.12214 | -2.93925 | -3.07781 |
| C | -0.49854 | -0.57207 | -2.41231 |
| H | 0.82351 | -3.33001 | -3.48347 |
| H | -0.72815 | -2.64302 | -3.94285 |
| C | -0.84008 | -4.07750 | -2.33053 |
| C | -0.25372 | 0.73528 | -1.70694 |
| H | 0.61060 | 0.65216 | -1.04555 |
| C | -1.43802 | 1.26988 | -0.88170 |
| H | 0.00058 | 1.49334 | -2.46272 |
| C | -1.22367 | 2.69487 | -0.29608 |
| O | -1.67526 | 0.36015 | 0.20103 |
| H | -2.32447 | 1.30077 | -1.53256 |
| Si | -3.15918 | -0.27290 | 0.67208 |
| C | 0.01025 | 2.77729 | 0.64224 |
| H | -2.10126 | 2.85089 | 0.34710 |
| C | -1.25349 | 3.82459 | -1.34828 |
| H | -0.44434 | 3.69483 | -2.07840 |
| H | -1.03377 | 4.76792 | -0.82926 |
| C | -2.58638 | 3.98201 | -2.09252 |
| H | -3.42063 | 4.10526 | -1.39040 |
| H | -2.81375 | 3.12012 | -2.72968 |
| H | -2.56625 | 4.86602 | -2.73994 |
| H | 0.08203 | 1.81188 | 1.15779 |
| H | -0.20183 | 3.51610 | 1.42780 |
| C | 1.37017 | 3.14582 | 0.01398 |
| C | 2.56512 | 2.77003 | 0.90537 |
| H | 1.51837 | 2.65934 | -0.95472 |
| H | 1.40992 | 4.22645 | -0.17559 |
| H | 3.49065 | 3.16485 | 0.48065 |
| N | 2.76142 | 1.32830 | 1.02518 |
| H | 2.44335 | 3.19408 | 1.91100 |
| H | 2.12175 | 0.79786 | 1.59847 |
| C | 3.73680 | 0.64983 | 0.34362 |
| O | 4.54540 | 1.21212 | -0.38948 |
| C | 3.78084 | -0.86655 | 0.57572 |
| C | 5.01797 | -1.21695 | 1.43477 |
| H | 2.88235 | -1.18032 | 1.12714 |
| C | 4.97685 | -0.66901 | 2.86511 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 5.90769 | -0.83784 | 0.91717 | C | -3.01429 | -1.21541 | -2.26276 |
| H | 5.11199 | -2.31050 | 1.46721 | H | -4.10214 | -2.00665 | 0.97671 |
| H | 5.86844 | -0.97414 | 3.42431 | H | -2.60797 | -2.38544 | 0.16031 |
| H | 4.10100 | -1.04307 | 3.41107 | C | -2.04210 | -0.06299 | -2.47502 |
| H | 4.93683 | 0.42585 | 2.87891 | C | -2.56595 | 1.15853 | -3.21369 |
| H | 2.59701 | -0.31461 | -1.98707 | C | -0.73632 | -0.13118 | -2.16478 |
| H | 2.87756 | -1.89812 | -2.67720 | H | -2.95038 | 0.83627 | -4.19429 |
| H | 1.03257 | -1.32127 | -0.29045 | H | -1.72484 | 1.83106 | -3.42254 |
| H | 1.38612 | -2.92038 | -0.91312 | C | -3.67147 | 1.96175 | -2.50704 |
| H | -1.27349 | -0.55105 | -3.18185 | C | -0.00647 | -1.28454 | -1.51184 |
| H | -0.27076 | -4.41496 | -1.45715 | H | -0.55271 | -1.63808 | -0.63330 |
| H | -0.98337 | -4.94343 | -2.98735 | C | 1.43354 | -0.93136 | -1.10463 |
| H | -1.82582 | -3.75282 | -1.97893 | H | 0.03931 | -2.13947 | -2.20276 |
| C | -4.33233 | 1.10708 | 1.22906 | C | 2.23955 | -2.11170 | -0.49256 |
| C | -3.97291 | -1.18178 | -0.77337 | O | 1.39500 | 0.20547 | -0.21633 |
| C | -2.74364 | -1.45345 | 2.12089 | H | 1.96572 | -0.63436 | -2.02067 |
| H | -3.29740 | -1.92419 | -1.21083 | Si | 2.41763 | 1.55367 | -0.30295 |
| H | -4.25505 | -0.48424 | -1.57158 | C | 1.64950 | -2.72229 | 0.80270 |
| H | -4.88903 | -1.69583 | -0.45784 | H | 3.22783 | -1.69614 | -0.24435 |
| H | -3.93838 | 1.66830 | 2.08403 | C | 2.46722 | -3.20503 | -1.56618 |
| H | -5.31112 | 0.70371 | 1.51683 | H | 2.58047 | -2.73076 | -2.55142 |
| H | -4.50530 | 1.82312 | 0.41640 | H | 1.57468 | -3.84148 | -1.63790 |
| C | -1.85610 | -2.61319 | 1.62191 | C | 3.69809 | -4.08359 | -1.31018 |
| C | -4.04569 | -2.03432 | 2.71486 | H | 3.63710 | -4.60805 | -0.34995 |
| C | -1.98702 | -0.68492 | 3.22537 | H | 4.61576 | -3.48270 | -1.30139 |
| H | -4.61605 | -2.61095 | 1.97588 | H | 3.80573 | -4.84397 | -2.09194 |
| H | -4.70388 | -1.25076 | 3.10929 | H | 2.11658 | -3.70264 | 0.95110 |
| H | -3.81461 | -2.71448 | 3.54740 | H | 0.58476 | -2.93251 | 0.64699 |
| H | -0.92252 | -2.24667 | 1.18107 | C | 1.83015 | -1.88962 | 2.10005 |
| H | -2.36510 | -3.22147 | 0.86471 | C | 0.52764 | -1.63465 | 2.86863 |
| H | -1.59432 | -3.28130 | 2.45591 | H | 2.29360 | -0.92710 | 1.86591 |
| H | -1.04511 | -0.26836 | 2.85149 | H | 2.52144 | -2.40090 | 2.78139 |
| H | -1.74815 | -1.35594 | 4.06363 | H | 0.05598 | -2.57260 | 3.17968 |
| H | -2.58060 | 0.14360 | 3.63084 | N | -0.43649 | -0.91825 | 2.04110 |
| | | | | H | 0.74360 | -1.07144 | 3.78765 |
| | | | | H | -0.07074 | -0.35641 | 1.27935 |
| | | | | C | -1.78397 | -1.06795 | 2.19782 |
| | | | | O | -2.27303 | -1.72473 | 3.11483 |
| | | | | C | -2.66039 | -0.42422 | 1.11657 |
| | | | | C | -3.70476 | 0.50201 | 1.76916 |
| | | | | H | -2.03362 | 0.16393 | 0.43422 |
| | | | | C | -3.10017 | 1.73412 | 2.45013 |
| | | | | H | -4.26007 | -0.08988 | 2.50658 |
| | | | | H | -4.42662 | 0.82449 | 1.00771 |
| | | | | H | -3.88180 | 2.35958 | 2.89638 |
| | | | | H | -2.54361 | 2.35514 | 1.73693 |
| | | | | H | -2.41063 | 1.44504 | 3.25153 |
| | | | | H | -4.74669 | -1.94140 | -1.24516 |

---

Compound **5.26**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in toluene was used.

Electronic Energy: -1476.97402529 hartree.
Free Energy: -1476.328544 hartree.

| | | | |
|---|---|---|---|
| C | -3.96248 | -1.20260 | -1.03219 |
| C | -3.33322 | -1.57657 | 0.32399 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -4.47791 | -0.23925 | -0.95633 | H | -0.28752 | 3.41937 | -2.09866 |
| H | -3.65283 | -1.26436 | -3.15701 | H | 1.45048 | 3.68077 | -2.00304 |
| H | -2.45989 | -2.16292 | -2.24364 | C | 0.28596 | 5.09395 | -0.86267 |
| H | -0.11512 | 0.72542 | -2.42323 | C | -0.51951 | 0.69337 | 0.93893 |
| H | -3.91661 | 2.85970 | -3.08628 | H | 0.45197 | 0.43149 | 1.36840 |
| H | -3.35214 | 2.28185 | -1.50879 | C | -1.23732 | -0.59953 | 0.47780 |
| H | -4.59415 | 1.38318 | -2.39746 | H | -1.11261 | 1.09569 | 1.77334 |
| C | 4.09178 | 1.17188 | 0.49550 | C | -0.49777 | -1.38592 | -0.63598 |
| C | 2.73232 | 2.02627 | -2.10967 | O | -2.55052 | -0.26636 | 0.00456 |
| C | 1.52008 | 2.96672 | 0.62843 | H | -1.32342 | -1.25204 | 1.35995 |
| H | 1.80715 | 2.22976 | -2.65997 | Si | -3.98564 | -0.14693 | 0.87078 |
| H | 3.27611 | 1.24414 | -2.65203 | C | 0.91534 | -1.81804 | -0.18017 |
| H | 3.34996 | 2.93140 | -2.15551 | H | -0.37745 | -0.68708 | -1.47761 |
| H | 3.99356 | 0.86740 | 1.54334 | C | -1.33580 | -2.57610 | -1.16200 |
| H | 4.74573 | 2.05212 | 0.46521 | H | -0.87189 | -2.94765 | -2.08491 |
| H | 4.61149 | 0.36504 | -0.03517 | H | -2.31988 | -2.19665 | -1.45244 |
| C | 2.39545 | 4.24050 | 0.59199 | C | -1.51689 | -3.75450 | -0.19584 |
| C | 1.27260 | 2.58267 | 2.10332 | H | -1.98037 | -3.45000 | 0.74952 |
| C | 0.16747 | 3.27270 | -0.04967 | H | -0.56667 | -4.24339 | 0.04943 |
| H | 0.77609 | 3.40919 | 2.63191 | H | -2.16620 | -4.51729 | -0.64294 |
| H | 2.20898 | 2.37448 | 2.63539 | H | 0.84309 | -2.45460 | 0.71294 |
| H | 0.62853 | 1.70229 | 2.19988 | H | 1.48138 | -0.93578 | 0.13132 |
| H | 2.58821 | 4.58402 | -0.43168 | C | 1.73298 | -2.55605 | -1.25209 |
| H | 3.36380 | 4.09139 | 1.08498 | C | 3.20665 | -2.77542 | -0.86804 |
| H | 1.88712 | 5.06102 | 1.11799 | H | 1.29586 | -3.54136 | -1.45685 |
| H | 0.29671 | 3.60419 | -1.08741 | H | 1.69267 | -2.00076 | -2.20132 |
| H | -0.35424 | 4.07853 | 0.48675 | H | 3.28645 | -3.20769 | 0.13258 |
| H | -0.49129 | 2.39762 | -0.06065 | N | 3.99458 | -1.54798 | -0.85234 |
| ---------- | | | | H | 3.66926 | -3.47652 | -1.57416 |
| | | | | H | 4.16088 | -1.08575 | -1.73631 |
| Compound **5.26** | | | | C | 4.45168 | -0.94628 | 0.28355 |
| This structure was assigned as incorrect. | | | | O | 4.27473 | -1.41928 | 1.40613 |
| B3LYP/6-31g(d) | | | | C | 5.17871 | 0.39313 | 0.08451 |
| SMD implicit solvation in toluene was used. | | | | C | 6.53897 | 0.37077 | 0.80672 |
| | | | | H | 5.35515 | 0.55810 | -0.98908 |
| | | | | C | 7.53158 | -0.64677 | 0.23721 |
| Electronic Energy: -1476.98461226 hartree. | | | | H | 6.36113 | 0.15777 | 1.86738 |
| | | | | H | 6.97532 | 1.37675 | 0.75087 |
| Free Energy: -1476.344128 hartree. | | | | H | 8.48874 | -0.59873 | 0.76967 |
| | | | | H | 7.73505 | -0.45904 | -0.82517 |
| C | 2.99779 | 1.73115 | -0.22321 | H | 7.15606 | -1.67259 | 0.33064 |
| C | 4.26821 | 1.52644 | 0.61531 | H | 2.55533 | 0.75775 | -0.45960 |
| C | 1.91477 | 2.58314 | 0.47086 | H | 3.26371 | 2.18284 | -1.18955 |
| H | 4.84520 | 2.46012 | 0.65466 | H | 1.74060 | 2.17913 | 1.47457 |
| H | 3.99596 | 1.27959 | 1.64962 | H | 2.29366 | 3.60394 | 0.61631 |
| C | 0.62067 | 2.61573 | -0.32395 | H | -1.27098 | 1.85462 | -0.76536 |
| C | 0.52519 | 3.67506 | -1.40775 | H | -0.66240 | 5.14739 | -0.31521 |
| C | -0.39525 | 1.75811 | -0.12385 | H | 0.24676 | 5.82418 | -1.68030 |

| | | | |
|---|---|---|---|
| H | 1.08306 | 5.40879 | -0.17875 |
| C | -4.31077 | -1.73733 | 1.84321 |
| C | -3.93209 | 1.28265 | 2.11184 |
| C | -5.33435 | 0.15449 | -0.45953 |
| H | -3.63531 | 2.23041 | 1.64793 |
| H | -3.22636 | 1.07851 | 2.92694 |
| H | -4.91429 | 1.43644 | 2.57808 |
| H | -4.42720 | -2.61300 | 1.19463 |
| H | -5.22553 | -1.64607 | 2.44303 |
| H | -3.49561 | -1.95280 | 2.54576 |
| C | -5.31956 | -0.97990 | -1.50435 |
| C | -5.07919 | 1.49619 | -1.17804 |
| C | -6.72435 | 0.20027 | 0.21133 |
| H | -4.10067 | 1.51288 | -1.67191 |
| H | -5.12049 | 2.34766 | -0.48746 |
| H | -5.84142 | 1.67039 | -1.95251 |
| H | -5.48529 | -1.96511 | -1.05046 |
| H | -4.36842 | -1.01822 | -2.04667 |
| H | -6.11683 | -0.82974 | -2.24813 |
| H | -6.97851 | -0.74670 | 0.70379 |
| H | -7.50576 | 0.39361 | -0.53852 |
| H | -6.79724 | 0.99655 | 0.96274 |

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Compound **5.27**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -167.631134 kJ.

| | | | |
|---|---|---|---|
| C | 1.03870 | -9.56160 | -5.40960 |
| C | 2.01250 | -10.57890 | -6.04280 |
| C | 0.02060 | -8.97940 | -6.40990 |
| H | 2.45300 | -10.13560 | -6.93630 |
| H | 2.84680 | -10.74020 | -5.35740 |
| C | -1.39220 | -8.90270 | -5.85010 |
| C | -1.60190 | -7.89530 | -4.72780 |
| C | -2.36600 | -9.68680 | -6.35440 |
| H | -0.75090 | -7.93440 | -4.04760 |
| H | -2.46050 | -8.17130 | -4.11870 |
| C | -1.77820 | -6.46600 | -5.25400 |
| C | -3.83890 | -9.71690 | -5.97610 |
| C | -4.33810 | -11.09100 | -5.46740 |
| C | -4.22030 | -11.37690 | -3.94310 |
| O | -3.69660 | -12.11280 | -6.21420 |
| H | -5.40620 | -11.12710 | -5.69130 |
| Si | -4.48090 | -13.18100 | -7.26030 |
| C | -2.77020 | -11.64240 | -3.47840 |
| H | -4.78720 | -12.29320 | -3.76930 |
| C | -4.91640 | -10.28680 | -3.09810 |
| H | -5.83110 | -9.96870 | -3.60000 |
| H | -4.28390 | -9.40110 | -3.03320 |
| C | -5.29470 | -10.74680 | -1.68140 |
| H | -5.81230 | -9.95190 | -1.14370 |
| H | -4.41980 | -11.02050 | -1.09220 |
| H | -5.96010 | -11.61010 | -1.71040 |
| H | -2.62310 | -11.31180 | -2.45110 |
| H | -2.08920 | -11.02520 | -4.05880 |
| C | -2.37340 | -13.13220 | -3.55040 |
| C | -0.85730 | -13.35760 | -3.60270 |
| H | -2.79120 | -13.65500 | -2.68930 |
| H | -2.82340 | -13.60590 | -4.42180 |
| H | -0.37510 | -12.92130 | -2.72590 |
| N | -0.31110 | -12.76620 | -4.81360 |
| H | -0.63180 | -14.42530 | -3.59320 |
| H | -0.96510 | -12.32970 | -5.44740 |
| C | 0.99170 | -12.69800 | -5.09840 |
| O | 1.85550 | -13.18360 | -4.37080 |
| C | 1.37830 | -11.95080 | -6.38590 |
| C | 2.32620 | -12.79620 | -7.26820 |
| H | 0.47300 | -11.77730 | -6.96780 |
| C | 1.68530 | -14.07130 | -7.84280 |
| H | 3.21860 | -13.06480 | -6.70000 |
| H | 2.67750 | -12.18790 | -8.10190 |
| H | 2.38710 | -14.59850 | -8.48940 |
| H | 0.80050 | -13.83830 | -8.43500 |
| H | 1.38800 | -14.76310 | -7.05380 |
| H | 0.52850 | -10.01610 | -4.55940 |
| H | 1.61270 | -8.73770 | -4.98340 |
| H | 0.00730 | -9.57120 | -7.32530 |
| H | 0.33690 | -7.98450 | -6.72440 |
| H | -2.63640 | -6.39770 | -5.92310 |
| H | -1.94100 | -5.76780 | -4.43270 |
| H | -0.89800 | -6.13010 | -5.80240 |
| C | -5.55980 | -14.32860 | -6.22680 |
| C | -5.53510 | -12.17490 | -8.45760 |
| C | -3.14460 | -14.16210 | -8.20960 |
| H | -6.31420 | -11.61870 | -7.93910 |
| H | -6.02390 | -12.81510 | -9.19060 |
| H | -4.92850 | -11.45490 | -9.00510 |
| H | -4.96490 | -14.87100 | -5.49320 |
| H | -6.06580 | -15.06620 | -6.84820 |
| H | -6.32300 | -13.77520 | -5.68220 |
| C | -2.23070 | -13.17270 | -8.95210 |
| C | -3.82390 | -15.10430 | -9.21780 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.30870 | -14.98410 | -7.21480 | H | -0.15440 | -12.37750 | -9.06000 |
| H | -3.08920 | -15.68760 | -9.77360 | H | -0.96660 | -13.92220 | -7.66620 |
| H | -4.41800 | -14.55040 | -9.94520 | H | -2.58150 | -14.18590 | -7.13240 |
| H | -4.49020 | -15.80850 | -8.71840 | C | -1.10320 | -14.33650 | -5.56050 |
| H | -1.73280 | -12.49700 | -8.25610 | C | 0.43170 | -14.45800 | -5.50690 |
| H | -2.79320 | -12.56000 | -9.65710 | H | -1.51400 | -15.34390 | -5.48260 |
| H | -1.45630 | -13.69250 | -9.51650 | H | -1.45920 | -13.81450 | -4.67260 |
| H | -1.81970 | -14.34110 | -6.48470 | H | 0.72900 | -14.96770 | -4.58790 |
| H | -1.52780 | -15.55160 | -7.72180 | N | 1.11070 | -13.16980 | -5.59600 |
| H | -2.92490 | -15.69460 | -6.66330 | H | 0.78190 | -15.08680 | -6.32580 |
| H | -4.11120 | -8.91160 | -5.29830 | H | 1.46650 | -12.89300 | -6.49710 |
| H | -4.37300 | -9.49030 | -6.89920 | C | 1.32560 | -12.34720 | -4.56170 |
| H | -2.10820 | -10.37510 | -7.14550 | O | 0.90980 | -12.58900 | -3.43040 |
| | | | | C | 2.15090 | -11.07710 | -4.84400 |

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Compound **5.27**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -164.619034 kJ.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.55420 | -9.31970 | -3.72790 | C | 3.26860 | -10.84990 | -3.79840 |
| C | 1.24500 | -9.83430 | -5.01090 | H | 2.64560 | -11.22310 | -5.80520 |
| C | -0.47510 | -8.20620 | -4.00580 | C | 4.38710 | -11.90450 | -3.82920 |
| H | 0.49020 | -10.06240 | -5.76310 | H | 2.83900 | -10.81920 | -2.79570 |
| H | 1.83270 | -9.02250 | -5.44030 | H | 3.71580 | -9.86890 | -3.96070 |
| C | -1.66170 | -8.62490 | -4.87070 | H | 5.15890 | -11.66890 | -3.09600 |
| C | -2.11570 | -7.56510 | -5.86470 | H | 4.86410 | -11.95050 | -4.80830 |
| C | -2.25870 | -9.82840 | -4.73450 | H | 4.00630 | -12.89860 | -3.59170 |
| H | -2.10300 | -6.59390 | -5.36860 | H | 0.08510 | -10.13500 | -3.17920 |
| H | -3.15360 | -7.71830 | -6.15570 | H | 1.31260 | -8.92470 | -3.05140 |
| C | -1.22620 | -7.52540 | -7.11420 | H | -0.86630 | -7.81880 | -3.06440 |
| C | -3.40990 | -10.38800 | -5.55370 | H | 0.04210 | -7.37060 | -4.47840 |
| C | -3.19580 | -11.86800 | -5.93490 | H | -1.23750 | -8.48350 | -7.63350 |
| C | -1.91780 | -12.16820 | -6.76700 | H | -1.57300 | -6.76470 | -7.81370 |
| O | -4.32040 | -12.31340 | -6.67020 | H | -0.19050 | -7.29680 | -6.86290 |
| H | -3.14890 | -12.42770 | -5.00060 | C | -4.88550 | -14.83650 | -5.31930 |
| Si | -5.58560 | -13.23880 | -6.03920 | C | -6.45440 | -12.24560 | -4.69310 |
| C | -1.65150 | -13.69160 | -6.85220 | C | -6.78160 | -13.62090 | -7.47530 |
| H | -1.07680 | -11.71470 | -6.24740 | H | -6.80510 | -11.28850 | -5.07680 |
| C | -1.98010 | -11.53720 | -8.17780 | H | -5.78770 | -12.03930 | -3.85730 |
| H | -2.40660 | -10.53800 | -8.12180 | H | -7.31900 | -12.77840 | -4.30050 |
| H | -2.66480 | -12.10810 | -8.80660 | H | -5.67370 | -15.45930 | -4.89920 |
| C | -0.61150 | -11.40830 | -8.86560 | H | -4.16690 | -14.63760 | -4.52600 |
| H | -0.71340 | -10.90060 | -9.82500 | H | -4.37770 | -15.42480 | -6.08160 |
| H | 0.07960 | -10.82390 | -8.25770 | C | -7.95040 | -14.47810 | -6.96030 |
| | | | | C | -6.01470 | -14.38190 | -8.57010 |
| | | | | C | -7.31410 | -12.29530 | -8.04500 |
| | | | | H | -6.65050 | -14.59340 | -9.43000 |
| | | | | H | -5.63230 | -15.33440 | -8.20230 |
| | | | | H | -5.16000 | -13.80370 | -8.92540 |
| | | | | H | -8.50790 | -13.96270 | -6.17760 |
| | | | | H | -7.59910 | -15.42280 | -6.54450 |
| | | | | H | -8.65220 | -14.71370 | -7.76060 |
| | | | | H | -7.87150 | -11.73320 | -7.29510 |

| | | | |
|---|---|---|---|
| H | -7.97980 | -12.46270 | -8.89190 |
| H | -6.49710 | -11.65840 | -8.38790 |
| H | -4.31030 | -10.30060 | -4.94680 |
| H | -3.59520 | -9.79610 | -6.44620 |
| H | -1.90000 | -10.50450 | -3.97270 |

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Compound **5.27**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in toluene was used.

Electronic Energy: -1476.38515335 hartree.
Free Energy: -1475.739584 hartree.

| | | | |
|---|---|---|---|
| C | -3.59404 | 1.25307 | -1.23621 |
| C | -3.85631 | 0.80451 | 0.20044 |
| C | -2.86924 | 2.60694 | -1.32150 |
| H | -2.90499 | 0.79510 | 0.75013 |
| H | -4.50334 | 1.53619 | 0.70421 |
| C | -1.54593 | 2.59443 | -0.57947 |
| C | -1.53385 | 3.26119 | 0.77767 |
| C | -0.47596 | 2.00923 | -1.13048 |
| H | -0.77536 | 2.81633 | 1.43057 |
| H | -2.50288 | 3.09754 | 1.26639 |
| C | -1.28632 | 4.76910 | 0.65914 |
| C | 0.88419 | 1.83068 | -0.51891 |
| C | 1.19294 | 0.35579 | -0.21743 |
| C | 0.28013 | -0.27514 | 0.84463 |
| O | 2.54259 | 0.23335 | 0.21231 |
| H | 1.04569 | -0.20277 | -1.15876 |
| Si | 3.75603 | -0.33768 | -0.78889 |
| C | 0.45528 | -1.80306 | 0.84244 |
| H | -0.75358 | -0.03742 | 0.55180 |
| C | 0.54166 | 0.29299 | 2.24677 |
| H | 0.78912 | 1.35923 | 2.19143 |
| H | 1.42809 | -0.19797 | 2.66695 |
| C | -0.65220 | 0.11308 | 3.18168 |
| H | -0.43735 | 0.49336 | 4.18539 |
| H | -0.92962 | -0.94259 | 3.28938 |
| H | -1.52871 | 0.65463 | 2.80335 |
| H | 0.10810 | -2.21523 | 1.80046 |
| H | 1.53326 | -2.00721 | 0.81170 |
| C | -0.26673 | -2.53520 | -0.29965 |
| C | -1.63268 | -3.08949 | 0.10774 |
| H | 0.33774 | -3.38025 | -0.65108 |
| H | -0.40569 | -1.86811 | -1.16121 |
| H | -2.09437 | -3.61435 | -0.73140 |
| N | -2.58517 | -2.07478 | 0.52805 |
| H | -1.50808 | -3.80428 | 0.92996 |
| H | -2.53160 | -1.70906 | 1.46963 |
| C | -3.58625 | -1.63992 | -0.28412 |
| O | -3.71978 | -2.04241 | -1.43301 |
| C | -4.50988 | -0.58594 | 0.32825 |
| C | -5.89471 | -0.66085 | -0.31552 |
| H | -4.61001 | -0.80458 | 1.40137 |
| C | -6.63927 | -1.94261 | 0.04453 |
| H | -5.78082 | -0.60353 | -1.40222 |
| H | -6.47663 | 0.21381 | 0.00181 |
| H | -7.62725 | -1.97177 | -0.42533 |
| H | -6.78166 | -2.02871 | 1.12797 |
| H | -6.08240 | -2.82074 | -0.29777 |
| H | -2.98567 | 0.49574 | -1.74654 |
| H | -4.54108 | 1.31763 | -1.78546 |
| H | -2.70785 | 2.84907 | -2.37778 |
| H | -3.51628 | 3.39364 | -0.91096 |
| H | -2.02644 | 5.23759 | 0.00096 |
| H | -1.34595 | 5.25961 | 1.63587 |
| H | -0.29585 | 4.96348 | 0.23525 |
| C | 3.34870 | -2.06958 | -1.40061 |
| C | 3.93788 | 0.78501 | -2.28573 |
| C | 5.31396 | -0.33264 | 0.28556 |
| H | 4.09498 | 1.83045 | -1.99924 |
| H | 3.04510 | 0.74317 | -2.92155 |
| H | 4.78743 | 0.48072 | -2.90927 |
| H | 2.35066 | -2.10999 | -1.85409 |
| H | 3.38107 | -2.81968 | -0.60251 |
| H | 4.06221 | -2.37660 | -2.17465 |
| C | 5.00084 | -0.98493 | 1.63815 |
| C | 5.77424 | 1.11292 | 0.51303 |
| C | 6.42940 | -1.11996 | -0.41421 |
| H | 6.64883 | 1.13801 | 1.17840 |
| H | 4.98705 | 1.71922 | 0.97677 |
| H | 6.06388 | 1.59743 | -0.42722 |
| H | 4.66025 | -2.02165 | 1.52227 |
| H | 4.22092 | -0.43545 | 2.17574 |
| H | 5.89968 | -1.00541 | 2.27069 |
| H | 6.15840 | -2.17331 | -0.55423 |
| H | 7.35036 | -1.09475 | 0.18514 |
| H | 6.67255 | -0.70246 | -1.39958 |
| H | 1.65231 | 2.18110 | -1.22088 |
| H | 1.00513 | 2.42432 | 0.39195 |
| H | -0.59512 | 1.57627 | -2.12726 |

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Compound **5.27**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in toluene was used.

Electronic Energy: -1476.98121826 hartree.
Free Energy: -1476.340518 hartree.

| | | | |
|---|---|---|---|
| C | -3.61756 | 1.44758 | -1.17926 |
| C | -3.99545 | 0.91324 | 0.20921 |
| C | -2.82774 | 2.77359 | -1.12933 |
| H | -3.09278 | 0.87698 | 0.83234 |
| H | -4.68041 | 1.62000 | 0.69925 |
| C | -1.49818 | 2.68589 | -0.38027 |
| C | -1.38545 | 3.54058 | 0.86585 |
| C | -0.51863 | 1.89372 | -0.84831 |
| H | -0.55564 | 3.20918 | 1.49858 |
| H | -2.30071 | 3.41784 | 1.46279 |
| C | -1.20272 | 5.03702 | 0.55350 |
| C | 0.85343 | 1.64080 | -0.28166 |
| C | 1.16971 | 0.13704 | -0.10301 |
| C | 0.32958 | -0.55612 | 0.99847 |
| O | 2.56193 | -0.02021 | 0.19655 |
| H | 0.94014 | -0.35724 | -1.06022 |
| Si | 3.80391 | -0.39907 | -0.87055 |
| C | 0.39215 | -2.09583 | 0.85272 |
| H | -0.70702 | -0.23331 | 0.83368 |
| C | 0.74914 | -0.11995 | 2.42042 |
| H | 1.02437 | 0.94134 | 2.42318 |
| H | 1.65757 | -0.66330 | 2.70802 |
| C | -0.33862 | -0.33851 | 3.47825 |
| H | 0.01567 | -0.04536 | 4.47403 |
| H | -0.64902 | -1.38891 | 3.54425 |
| H | -1.23228 | 0.26115 | 3.26070 |
| H | 0.11244 | -2.56645 | 1.80547 |
| H | 1.44307 | -2.36693 | 0.69317 |
| C | -0.47199 | -2.71066 | -0.26924 |
| C | -1.88860 | -3.14711 | 0.14129 |
| H | 0.02489 | -3.61393 | -0.64936 |
| H | -0.54995 | -2.02665 | -1.12363 |
| H | -2.35426 | -3.67627 | -0.69448 |
| N | -2.80918 | -2.07689 | 0.51516 |
| H | -1.82760 | -3.84350 | 0.98720 |
| H | -2.84136 | -1.78355 | 1.48179 |
| C | -3.71505 | -1.54496 | -0.35743 |
| O | -3.75431 | -1.87691 | -1.54263 |
| C | -4.66148 | -0.48883 | 0.23726 |
| C | -6.02659 | -0.52162 | -0.47011 |
| H | -4.82135 | -0.73746 | 1.29725 |
| C | -6.82919 | -1.79742 | -0.19868 |
| H | -5.86978 | -0.41720 | -1.54841 |
| H | -6.60618 | 0.35160 | -0.14098 |
| H | -7.80322 | -1.76235 | -0.70090 |
| H | -7.01570 | -1.93572 | 0.87452 |
| H | -6.30079 | -2.68348 | -0.56752 |
| H | -3.02594 | 0.69605 | -1.71416 |
| H | -4.52354 | 1.60572 | -1.77865 |
| H | -2.65465 | 3.10573 | -2.16159 |
| H | -3.45644 | 3.54520 | -0.66585 |
| H | -2.02270 | 5.42573 | -0.06199 |
| H | -1.17214 | 5.62707 | 1.47745 |
| H | -0.26746 | 5.21195 | 0.00927 |
| C | 3.63161 | -2.18231 | -1.47915 |
| C | 3.77117 | 0.72371 | -2.39360 |
| C | 5.40864 | -0.15166 | 0.14408 |
| H | 3.92865 | 1.78113 | -2.15161 |
| H | 2.81415 | 0.64525 | -2.92531 |
| H | 4.55130 | 0.43007 | -3.10803 |
| H | 2.69104 | -2.32652 | -2.02619 |
| H | 3.65065 | -2.91103 | -0.66021 |
| H | 4.44224 | -2.44274 | -2.17201 |
| C | 5.42954 | -1.10818 | 1.35480 |
| C | 5.48670 | 1.30149 | 0.65770 |
| C | 6.63903 | -0.44013 | -0.74331 |
| H | 6.40262 | 1.45106 | 1.24890 |
| H | 4.63416 | 1.55031 | 1.29978 |
| H | 5.50962 | 2.02969 | -0.16310 |
| H | 5.41424 | -2.16183 | 1.04879 |
| H | 4.57473 | -0.94060 | 2.01991 |
| H | 6.34417 | -0.95592 | 1.94719 |
| H | 6.64516 | -1.47049 | -1.12155 |
| H | 7.56687 | -0.30333 | -0.16821 |
| H | 6.69485 | 0.23294 | -1.60834 |
| H | 1.60537 | 2.03836 | -0.97745 |
| H | 1.01216 | 2.16412 | 0.66599 |
| H | -0.72122 | 1.34942 | -1.77460 |

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Compound **5.27**
This structure was assigned as correct.
B3LYP/6-31g(d)

SMD implicit solvation in toluene was used.

Electronic Energy: -1476.98117992 hartree.
Free Energy: -1476.341856 hartree.

| | | | |
|---|---|---|---|
| C | -3.96476 | 2.40334 | -0.35034 |
| C | -3.70919 | 1.09455 | -1.11431 |
| C | -3.10727 | 2.60004 | 0.92500 |
| H | -4.18164 | 1.14459 | -2.10262 |
| H | -2.63130 | 1.00662 | -1.29867 |
| C | -1.60449 | 2.52490 | 0.70627 |
| C | -0.99218 | 3.62681 | -0.13971 |
| C | -0.89149 | 1.53672 | 1.27842 |
| H | -1.63006 | 3.81781 | -1.01219 |
| H | -0.02273 | 3.31325 | -0.53923 |
| C | -0.80603 | 4.94726 | 0.63057 |
| C | 0.59043 | 1.27681 | 1.18979 |
| C | 0.97504 | -0.05498 | 0.49303 |
| C | 0.43705 | -1.32882 | 1.19354 |
| O | 2.40312 | -0.13902 | 0.41970 |
| H | 0.55239 | -0.02348 | -0.52221 |
| Si | 3.39858 | 0.28121 | -0.86868 |
| C | 0.60766 | -2.58286 | 0.30155 |
| H | -0.63434 | -1.15444 | 1.35583 |
| C | 1.08815 | -1.56024 | 2.57755 |
| H | 1.24017 | -0.60050 | 3.08479 |
| H | 2.09013 | -1.98263 | 2.43414 |
| C | 0.27346 | -2.46638 | 3.50818 |
| H | -0.71486 | -2.03651 | 3.71887 |
| H | 0.78394 | -2.59763 | 4.46985 |
| H | 0.11582 | -3.46634 | 3.08680 |
| H | 0.47060 | -3.48064 | 0.91959 |
| H | 1.65473 | -2.60803 | -0.02528 |
| C | -0.29636 | -2.73003 | -0.93829 |
| C | -1.75967 | -3.13733 | -0.67831 |
| H | 0.14000 | -3.51589 | -1.57033 |
| H | -0.29310 | -1.81775 | -1.54787 |
| H | -2.20320 | -3.50212 | -1.60793 |
| N | -2.62842 | -2.05969 | -0.22001 |
| H | -1.79902 | -3.95397 | 0.05436 |
| H | -2.56853 | -1.76554 | 0.74380 |
| C | -3.48090 | -1.38431 | -1.04550 |
| O | -3.63870 | -1.68111 | -2.22926 |
| C | -4.20772 | -0.19426 | -0.41109 |
| C | -5.73321 | -0.37511 | -0.53491 |
| H | -3.94647 | -0.14275 | 0.65507 |
| C | -6.29034 | -1.53457 | 0.29630 |
| H | -5.96911 | -0.53291 | -1.59432 |
| H | -6.22880 | 0.55670 | -0.23451 |
| H | -7.37720 | -1.61596 | 0.17733 |
| H | -6.08548 | -1.39803 | 1.36628 |
| H | -5.85448 | -2.49418 | -0.00675 |
| H | -3.78536 | 3.24004 | -1.03739 |
| H | -5.02225 | 2.47943 | -0.06444 |
| H | -3.37122 | 3.57937 | 1.35003 |
| H | -3.39644 | 1.85744 | 1.67909 |
| H | -1.75622 | 5.32655 | 1.02403 |
| H | -0.38677 | 5.72111 | -0.02351 |
| H | -0.12412 | 4.81551 | 1.47849 |
| C | 2.95177 | -0.73326 | -2.40110 |
| C | 3.20627 | 2.10945 | -1.31982 |
| C | 5.17339 | -0.09683 | -0.25548 |
| H | 3.44775 | 2.78115 | -0.48764 |
| H | 2.18066 | 2.33227 | -1.64093 |
| H | 3.86116 | 2.37566 | -2.15968 |
| H | 1.92722 | -0.52256 | -2.73301 |
| H | 3.02449 | -1.81298 | -2.22674 |
| H | 3.61169 | -0.48948 | -3.24370 |
| C | 5.33298 | -1.60543 | 0.02720 |
| C | 5.46028 | 0.68779 | 1.04230 |
| C | 6.19686 | 0.32096 | -1.33330 |
| H | 6.47756 | 0.47471 | 1.40336 |
| H | 4.76124 | 0.41868 | 1.84212 |
| H | 5.39219 | 1.77271 | 0.89138 |
| H | 5.17412 | -2.21368 | -0.87227 |
| H | 4.63127 | -1.95297 | 0.79407 |
| H | 6.34927 | -1.82314 | 0.38866 |
| H | 6.04851 | -0.21792 | -2.27790 |
| H | 7.22047 | 0.10114 | -0.99553 |
| H | 6.15420 | 1.39531 | -1.55176 |
| H | 1.09610 | 2.08049 | 0.64820 |
| H | 1.02519 | 1.27449 | 2.19846 |
| H | -1.44304 | 0.83358 | 1.90455 |

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Compound **5.27**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1476.95916371 hartree.
Free Energy: -1476.321313 hartree.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -3.89524 | 2.43214 | -0.42930 | H | -4.95889 | 2.55580 | -0.18753 |
| C | -3.65711 | 1.08856 | -1.13645 | H | -3.33492 | 3.63612 | 1.26604 |
| C | -3.07685 | 2.64324 | 0.86930 | H | -3.40201 | 1.92195 | 1.62910 |
| H | -4.09599 | 1.11325 | -2.14091 | H | -1.54395 | 5.29244 | 1.22995 |
| H | -2.57676 | 0.96120 | -1.27883 | H | -0.19375 | 5.70690 | 0.16355 |
| C | -1.57173 | 2.53968 | 0.69336 | H | 0.07379 | 4.66782 | 1.57705 |
| C | -0.91345 | 3.65937 | -0.09277 | C | 2.96084 | -0.88030 | -2.39037 |
| C | -0.89470 | 1.52130 | 1.25356 | C | 3.08808 | 2.02788 | -1.44475 |
| H | -1.56245 | 3.95216 | -0.92793 | C | 5.14680 | -0.04881 | -0.28103 |
| H | 0.02330 | 3.31897 | -0.54576 | H | 3.29555 | 2.73702 | -0.63556 |
| C | -0.62832 | 4.90389 | 0.76993 | H | 2.05370 | 2.18920 | -1.77304 |
| C | 0.58509 | 1.24335 | 1.19458 | H | 3.73641 | 2.28873 | -2.29033 |
| C | 0.96548 | -0.08855 | 0.49785 | H | 1.91152 | -0.77531 | -2.69159 |
| C | 0.45194 | -1.36145 | 1.21712 | H | 3.13566 | -1.93952 | -2.17066 |
| O | 2.39017 | -0.16636 | 0.40017 | H | 3.57369 | -0.61405 | -3.26017 |
| H | 0.52224 | -0.06461 | -0.50906 | C | 5.33064 | -1.52046 | 0.14754 |
| Si | 3.36239 | 0.23073 | -0.91180 | C | 5.42142 | 0.86256 | 0.93466 |
| C | 0.59430 | -2.61667 | 0.32250 | C | 6.15764 | 0.28138 | -1.40075 |
| H | -0.61304 | -1.18934 | 1.42269 | H | 6.44070 | 0.69786 | 1.31373 |
| C | 1.15555 | -1.59064 | 2.57540 | H | 4.72292 | 0.66062 | 1.75410 |
| H | 1.32905 | -0.62981 | 3.07333 | H | 5.33884 | 1.92566 | 0.67675 |
| H | 2.15076 | -2.01250 | 2.39066 | H | 5.17238 | -2.21381 | -0.68766 |
| C | 0.37424 | -2.49487 | 3.53724 | H | 4.63669 | -1.79590 | 0.94937 |
| H | -0.60383 | -2.06120 | 3.78310 | H | 6.35273 | -1.68569 | 0.51870 |
| H | 0.92016 | -2.62803 | 4.47819 | H | 6.01832 | -0.35475 | -2.28376 |
| H | 0.19721 | -3.49303 | 3.12041 | H | 7.18604 | 0.12233 | -1.04545 |
| H | 0.45079 | -3.51196 | 0.94277 | H | 6.08598 | 1.32660 | -1.72612 |
| H | 1.63849 | -2.65466 | -0.01256 | H | 1.10978 | 2.04324 | 0.66567 |
| C | -0.32279 | -2.75289 | -0.90912 | H | 1.00249 | 1.23224 | 2.21054 |
| C | -1.79346 | -3.12227 | -0.63534 | H | -1.47632 | 0.80961 | 1.84189 |
| H | 0.09156 | -3.55463 | -1.53591 | ---------- | | | |
| H | -0.30206 | -1.84793 | -1.52931 | | | | |
| H | -2.25594 | -3.48048 | -1.55812 | Compound **5.27** | | | |
| N | -2.63534 | -2.02066 | -0.18657 | This structure was assigned as correct. | | | |
| H | -1.84474 | -3.93465 | 0.10235 | M06-2X/6-31g(d) | | | |
| H | -2.51533 | -1.66594 | 0.74995 | SMD implicit solvation in toluene was used. | | | |
| C | -3.53350 | -1.39086 | -1.00550 | | | | |
| O | -3.75419 | -1.75544 | -2.15675 | | | | |
| C | -4.21824 | -0.15833 | -0.40540 | Electronic Energy: -1476.38318435 hartree. | | | |
| C | -5.74675 | -0.28119 | -0.54449 | | | | |
| H | -3.96507 | -0.09039 | 0.66270 | Free Energy: -1475.740345 hartree. | | | |
| C | -6.35536 | -1.40382 | 0.30231 | | | | |
| H | -5.97080 | -0.45409 | -1.60365 | C | 3.15491 | 0.23549 | -1.79503 |
| H | -6.21052 | 0.67466 | -0.26975 | C | 2.55278 | -1.05962 | -1.24897 |
| H | -7.44272 | -1.44727 | 0.17399 | C | 2.14867 | 1.01847 | -2.65698 |
| H | -6.15372 | -1.25509 | 1.37101 | H | 1.56347 | -0.84291 | -0.82333 |
| H | -5.95001 | -2.38134 | 0.01697 | H | 2.38985 | -1.75938 | -2.07992 |
| H | -3.65907 | 3.23688 | -1.13754 | C | 1.14633 | 1.80922 | -1.84488 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 1.65061 | 3.13523 | -1.31763 | C | -4.44471 | -0.59250 | 1.35901 |
| C | -0.10329 | 1.36792 | -1.65663 | C | -4.47446 | 0.00205 | -1.64873 |
| H | 2.71937 | 3.04712 | -1.08484 | C | -3.05397 | -2.57933 | -0.60946 |
| H | 1.15249 | 3.39754 | -0.37780 | H | -3.95464 | -0.08762 | -2.60920 |
| C | 1.44921 | 4.26469 | -2.33360 | H | -4.64388 | 1.06976 | -1.46360 |
| C | -1.23269 | 2.09518 | -0.97696 | H | -5.46141 | -0.46286 | -1.75519 |
| C | -1.87349 | 1.36098 | 0.21429 | H | -3.86936 | -0.96875 | 2.21184 |
| C | -1.14205 | 1.47529 | 1.56166 | H | -5.39458 | -1.13938 | 1.32982 |
| O | -2.00779 | -0.01752 | -0.11083 | H | -4.68580 | 0.45820 | 1.56140 |
| H | -2.87230 | 1.80198 | 0.36071 | C | -2.00881 | -2.63227 | -1.73158 |
| Si | -3.49129 | -0.77545 | -0.24997 | C | -4.30596 | -3.35222 | -1.04357 |
| C | 0.23484 | 0.79671 | 1.55846 | C | -2.46676 | -3.22376 | 0.65325 |
| H | -1.78364 | 0.91666 | 2.26408 | H | -4.06272 | -4.41011 | -1.21574 |
| C | -1.05018 | 2.91756 | 2.07750 | H | -4.72241 | -2.95655 | -1.97756 |
| H | -0.38782 | 3.49948 | 1.42281 | H | -5.09591 | -3.32009 | -0.28238 |
| H | -0.55418 | 2.89540 | 3.05575 | H | -1.08598 | -2.11825 | -1.44078 |
| C | -2.39213 | 3.63390 | 2.21807 | H | -2.37578 | -2.16676 | -2.65480 |
| H | -2.27215 | 4.59066 | 2.73553 | H | -1.75718 | -3.67576 | -1.96904 |
| H | -3.10170 | 3.02931 | 2.79588 | H | -1.60021 | -2.66239 | 1.02535 |
| H | -2.84916 | 3.84605 | 1.24578 | H | -2.13360 | -4.24926 | 0.43997 |
| H | 1.00604 | 1.50528 | 1.22129 | H | -3.20505 | -3.28002 | 1.46178 |
| H | 0.22717 | -0.01946 | 0.82933 | H | -0.93610 | 3.10303 | -0.66654 |
| C | 0.60815 | 0.23557 | 2.93229 | H | -2.02567 | 2.22846 | -1.72740 |
| C | 2.06204 | -0.22613 | 3.02189 | H | -0.38239 | 0.40849 | -2.09357 |
| H | -0.06222 | -0.60432 | 3.16566 | ---------- | | | |
| H | 0.44378 | 0.98492 | 3.71705 | | | | |
| H | 2.74407 | 0.62272 | 2.92956 | Compound **5.27** | | | |
| N | 2.40261 | -1.13444 | 1.94128 | This structure was assigned as incorrect. | | | |
| H | 2.25141 | -0.70121 | 3.99220 | B3LYP/6-31g(d) | | | |
| H | 1.73172 | -1.85221 | 1.69768 | Gas phase. | | | |
| C | 3.42449 | -0.89803 | 1.07502 | | | | |
| O | 4.26006 | -0.02096 | 1.25803 | Electronic Energy: -1476.95885877 hartree. | | | |
| C | 3.41328 | -1.76719 | -0.17935 | | | | |
| C | 4.83820 | -2.05408 | -0.65014 | Free Energy: -1476.319891 hartree. | | | |
| H | 2.92273 | -2.72020 | 0.06549 | | | | |
| C | 5.61551 | -2.92469 | 0.33213 | C | -3.74778 | 1.50249 | -1.20026 |
| H | 5.36048 | -1.10143 | -0.78284 | C | -3.99989 | 0.89287 | 0.18811 |
| H | 4.79275 | -2.54188 | -1.63239 | C | -3.00627 | 2.84834 | -1.12091 |
| H | 6.62800 | -3.12568 | -0.03139 | H | -3.06840 | 0.93024 | 0.76680 |
| H | 5.11888 | -3.88934 | 0.48792 | H | -4.72056 | 1.52341 | 0.72869 |
| H | 5.70408 | -2.42656 | 1.30319 | C | -1.55864 | 2.82140 | -0.63997 |
| H | 3.50434 | 0.86101 | -0.96425 | C | -1.10454 | 4.08524 | 0.06759 |
| H | 4.03821 | -0.00112 | -2.39962 | C | -0.75019 | 1.77430 | -0.86446 |
| H | 1.62625 | 0.32059 | -3.32354 | H | -1.52487 | 4.95365 | -0.46013 |
| H | 2.70153 | 1.71471 | -3.30216 | H | -0.01655 | 4.19324 | 0.00848 |
| H | 0.38414 | 4.41877 | -2.53676 | C | -1.53847 | 4.14747 | 1.54387 |
| H | 1.86712 | 5.20756 | -1.96659 | C | 0.70162 | 1.62945 | -0.47586 |
| H | 1.93645 | 4.03029 | -3.28621 | C | 1.09318 | 0.16948 | -0.16764 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 0.30780 | -0.46322 | 1.00727 | H | 2.55195 | -2.04973 | -2.25749 |
| O | 2.49359 | 0.10026 | 0.11500 | H | 3.41556 | -2.78560 | -0.90169 |
| H | 0.87113 | -0.42018 | -1.07140 | C | 6.56460 | -0.56913 | -0.66003 |
| Si | 3.74793 | -0.28761 | -0.93162 | C | 5.17647 | -1.23661 | 1.32886 |
| C | 0.45144 | -2.00321 | 0.99024 | C | 5.46961 | 1.19303 | 0.76478 |
| H | -0.74838 | -0.21488 | 0.83920 | H | 6.05921 | -1.18999 | 1.98364 |
| C | 0.72362 | 0.12712 | 2.37207 | H | 5.09765 | -2.26835 | 0.96432 |
| H | 0.89266 | 1.20617 | 2.27285 | H | 4.29382 | -1.02929 | 1.94370 |
| H | 1.69016 | -0.29879 | 2.66780 | H | 6.71812 | 0.13516 | -1.48698 |
| C | -0.30844 | -0.09750 | 3.48453 | H | 6.51196 | -1.57906 | -1.08556 |
| H | 0.03341 | 0.33553 | 4.43173 | H | 7.46437 | -0.52944 | -0.02907 |
| H | -1.26775 | 0.37345 | 3.23343 | H | 5.60892 | 1.94978 | -0.01700 |
| H | -0.49777 | -1.16249 | 3.66593 | H | 6.35074 | 1.23694 | 1.42176 |
| H | 0.16657 | -2.41125 | 1.96993 | H | 4.59461 | 1.48042 | 1.35797 |
| H | 1.51838 | -2.23288 | 0.87787 | H | 1.34546 | 1.96379 | -1.30266 |
| C | -0.35255 | -2.73875 | -0.10329 | H | 0.96207 | 2.26001 | 0.38019 |
| C | -1.75734 | -3.21124 | 0.30446 | H | -1.15837 | 0.91978 | -1.40529 |
| H | 0.19486 | -3.64019 | -0.41086 | ---------- | | | |
| H | -0.44947 | -2.12323 | -1.00505 | | | | |
| H | -2.18654 | -3.78959 | -0.52002 | Compound **5.28** | | | |
| N | -2.71932 | -2.16131 | 0.63496 | This structure was assigned as incorrect. | | | |
| H | -1.68744 | -3.87134 | 1.17749 | | | | |
| H | -2.90354 | -1.96124 | 1.60699 | Molecular Mechanics (OPLS-2005), gas | | | |
| C | -3.48066 | -1.54277 | -0.31721 | phase. | | | |
| O | -3.31758 | -1.75941 | -1.51705 | Energy: -198.863434 kJ. | | | |
| C | -4.53756 | -0.56153 | 0.21101 | | | | |
| C | -5.85445 | -0.72960 | -0.56760 | O | -1.41810 | -5.11170 | 15.46650 |
| H | -4.73431 | -0.80602 | 1.26634 | C | -1.70960 | -4.28980 | 14.35160 |
| C | -6.53262 | -2.08442 | -0.33974 | C | -3.05840 | -3.60070 | 14.57180 |
| H | -5.64645 | -0.60393 | -1.63501 | C | -1.63110 | -5.18730 | 13.08890 |
| H | -6.53657 | 0.07917 | -0.27190 | H | -0.93670 | -3.52330 | 14.26800 |
| H | -7.47860 | -2.14652 | -0.88923 | Si | -0.53730 | -4.62040 | 16.81970 |
| H | -6.75427 | -2.24930 | 0.72262 | H | -2.35460 | -5.98220 | 13.25650 |
| H | -5.89564 | -2.90611 | -0.68529 | C | -0.24870 | -5.86840 | 12.98280 |
| H | -3.20233 | 0.79171 | -1.82926 | C | -3.13730 | -2.25770 | 14.57910 |
| H | -4.70654 | 1.67109 | -1.70658 | C | -4.23150 | -4.53900 | 14.87320 |
| H | -3.03181 | 3.33051 | -2.11071 | C | -0.51040 | -6.08900 | 18.03640 |
| H | -3.57829 | 3.52119 | -0.46500 | C | 1.21030 | -4.18430 | 16.26200 |
| H | -1.08009 | 3.33589 | 2.12018 | C | -1.37780 | -3.12510 | 17.60110 |
| H | -1.24024 | 5.09852 | 2.00015 | H | 1.84190 | -3.91680 | 17.10780 |
| H | -2.62576 | 4.05474 | 1.64787 | H | 1.68060 | -5.02490 | 15.75400 |
| C | 3.47897 | -2.00936 | -1.67247 | H | 1.21140 | -3.34240 | 15.57170 |
| C | 3.85588 | 0.94936 | -2.36153 | H | -1.35390 | -2.26250 | 16.93770 |
| C | 5.31063 | -0.22369 | 0.17193 | H | -0.89440 | -2.83660 | 18.53310 |
| H | 3.98013 | 1.97912 | -2.00821 | H | -2.42300 | -3.33630 | 17.82340 |
| H | 2.94888 | 0.91738 | -2.97752 | H | -4.04580 | -1.72250 | 14.79700 |
| H | 4.70123 | 0.71826 | -3.02159 | H | -2.26180 | -1.65540 | 14.38420 |
| H | 4.29822 | -2.27799 | -2.35063 | C | -5.64490 | -3.92540 | 15.07090 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.95820 | -5.07170 | 15.78480 | H | -2.91010 | -3.85300 | 11.95910 |
| H | -4.28150 | -5.30360 | 14.10160 | H | -3.98310 | -6.43140 | 11.37300 |
| H | -5.55100 | -3.14400 | 15.82610 | H | -2.46010 | -7.31340 | 11.45830 |
| C | -6.58240 | -4.96510 | 15.72160 | H | -3.30390 | -7.18750 | 9.94000 |
| C | -6.27030 | -3.24320 | 13.81320 | H | -0.16750 | -3.98920 | 11.43080 |
| O | -7.66450 | -3.03610 | 14.02180 | H | -0.17330 | -6.49660 | 12.09610 |
| C | -6.08140 | -3.90750 | 12.43090 | H | 0.56080 | -5.13930 | 12.95370 |
| H | -5.81320 | -2.25910 | 13.74930 | H | -0.06730 | -6.51260 | 13.84360 |
| H | -7.54510 | -4.52570 | 15.98390 | C | 0.29450 | -5.70720 | 19.29050 |
| H | -6.15480 | -5.35230 | 16.64650 | H | 0.32820 | -6.52970 | 20.00540 |
| H | -6.77910 | -5.81710 | 15.07540 | H | 1.32400 | -5.44860 | 19.04030 |
| C | -6.68610 | -5.32240 | 12.32220 | H | -0.14450 | -4.84900 | 19.80040 |
| H | -5.01680 | -3.98820 | 12.24570 | C | 0.14090 | -7.29780 | 17.34310 |
| C | -6.68190 | -2.92270 | 11.40110 | H | 1.17260 | -7.08790 | 17.05940 |
| O | -8.06510 | -2.80290 | 11.72710 | H | 0.15060 | -8.17330 | 17.99270 |
| C | -6.52880 | -3.28890 | 9.90110 | H | -0.39860 | -7.56770 | 16.43390 |
| H | -6.20470 | -1.94960 | 11.52160 | C | -1.95750 | -6.43490 | 18.42660 |
| H | -6.17960 | -6.02580 | 12.97860 | H | -2.44750 | -5.59860 | 18.92630 |
| H | -6.58880 | -5.72740 | 11.31670 | H | -2.55410 | -6.68210 | 17.54690 |
| H | -7.74550 | -5.32270 | 12.57980 | H | -1.99630 | -7.28960 | 19.10220 |
| H | -6.89090 | -4.30230 | 9.73800 | | | | |
| C | -5.05750 | -3.25270 | 9.44880 | --- | | | |
| C | -7.38460 | -2.35890 | 9.01580 | | | | |
| C | -8.36040 | -2.35280 | 13.01890 | Compound **5.28** | | | |
| C | -9.83990 | -2.66780 | 13.24470 | This structure was assigned as ambiguous. | | | |
| C | -8.11490 | -0.83510 | 13.13450 | | | | |
| H | -7.06680 | -0.57590 | 13.00370 | Molecular Mechanics (OPLS-2005), gas | | | |
| H | -8.43030 | -0.48720 | 14.11820 | phase. | | | |
| H | -8.69590 | -0.31090 | 12.37560 | Energy: -185.219220 kJ. | | | |
| H | -10.00200 | -3.74270 | 13.16220 | | | | |
| H | -10.45000 | -2.16160 | 12.49660 | O | -1.94690 | -5.11110 | 14.97560 |
| H | -10.14630 | -2.34150 | 14.23860 | C | -3.10640 | -5.52210 | 14.26990 |
| H | -8.44730 | -2.50080 | 9.21180 | C | -4.09880 | -6.27340 | 15.15360 |
| H | -7.22110 | -2.55560 | 7.95570 | C | -2.67830 | -6.31360 | 13.00870 |
| H | -7.15090 | -1.30970 | 9.20020 | H | -3.61560 | -4.61470 | 13.96250 |
| O | -4.57890 | -2.27520 | 8.87230 | Si | -1.74400 | -3.56970 | 15.64300 |
| O | -4.38610 | -4.37960 | 9.74980 | H | -3.59890 | -6.69870 | 12.58650 |
| C | -3.00490 | -4.51860 | 9.41710 | C | -1.80330 | -7.53910 | 13.34330 |
| C | -2.88260 | -5.15020 | 8.01840 | C | -3.75960 | -6.72540 | 16.37340 |
| C | -2.28470 | -5.33150 | 10.52730 | C | -5.50240 | -6.50550 | 14.59300 |
| H | -2.53230 | -3.53560 | 9.37300 | C | -0.00560 | -3.51830 | 16.42160 |
| C | -2.01620 | -4.44280 | 11.77860 | C | -1.89890 | -2.30140 | 14.25750 |
| H | -1.31470 | -5.63440 | 10.13110 | C | -3.07870 | -3.28320 | 16.94260 |
| C | -3.05180 | -6.63560 | 10.84400 | H | -1.19870 | -2.50670 | 13.44760 |
| H | -1.83810 | -5.30340 | 7.74750 | H | -1.68890 | -1.29440 | 14.61490 |
| H | -3.32000 | -4.49720 | 7.26260 | H | -2.89590 | -2.28750 | 13.82260 |
| H | -3.39320 | -6.11010 | 7.95370 | H | -4.07740 | -3.34460 | 16.51420 |
| O | -0.98700 | -3.51960 | 11.47570 | H | -2.97830 | -2.30260 | 17.40550 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.02070 | -4.02630 | 17.73650 | H | -1.22230 | -5.14220 | 7.85890 |
| H | -4.46580 | -7.25670 | 16.99370 | H | -2.24910 | -3.75160 | 7.53940 |
| H | -2.76660 | -6.57460 | 16.77160 | H | -2.96110 | -5.35300 | 7.64010 |
| C | -6.52310 | -5.36740 | 14.83600 | O | -0.70140 | -5.15800 | 12.27240 |
| H | -5.87720 | -7.40440 | 15.08420 | H | -2.53570 | -4.40320 | 12.07240 |
| H | -5.47850 | -6.77180 | 13.53950 | H | -4.25150 | -6.50470 | 10.36670 |
| H | -6.41170 | -5.07900 | 15.88280 | H | -3.05150 | -7.77030 | 10.64370 |
| C | -7.96380 | -5.92040 | 14.74820 | H | -3.24570 | -7.09450 | 9.05320 |
| C | -6.30670 | -4.05160 | 14.02370 | H | -0.65310 | -5.13340 | 13.22120 |
| O | -7.45770 | -3.23480 | 14.21890 | H | -2.34420 | -8.24850 | 13.96910 |
| C | -6.00140 | -4.11840 | 12.49900 | H | -0.89920 | -7.25580 | 13.88240 |
| H | -5.47090 | -3.54410 | 14.50290 | H | -1.49430 | -8.06360 | 12.43960 |
| H | -8.70450 | -5.16590 | 15.01350 | C | 0.24470 | -2.12700 | 17.02750 |
| H | -8.10610 | -6.74670 | 15.44480 | H | 1.23190 | -2.06590 | 17.48640 |
| H | -8.21640 | -6.29150 | 13.75840 | H | 0.18860 | -1.34580 | 16.26860 |
| C | -7.07670 | -4.85970 | 11.68150 | H | -0.48970 | -1.88920 | 17.79790 |
| H | -5.06710 | -4.64920 | 12.33660 | C | 1.03780 | -3.81080 | 15.32960 |
| C | -5.80880 | -2.65140 | 12.03750 | H | 0.99530 | -3.07380 | 14.52660 |
| O | -7.03780 | -1.98100 | 12.29880 | H | 2.05090 | -3.79750 | 15.73220 |
| C | -5.38320 | -2.41540 | 10.56120 | H | 0.87750 | -4.79170 | 14.88000 |
| H | -5.03140 | -2.19420 | 12.64910 | C | 0.08080 | -4.59240 | 17.51910 |
| H | -7.09980 | -5.91840 | 11.92990 | H | -0.64050 | -4.40920 | 18.31600 |
| H | -6.88440 | -4.80990 | 10.61170 | H | -0.12380 | -5.58560 | 17.11600 |
| H | -8.06890 | -4.44420 | 11.86060 | H | 1.07150 | -4.61940 | 17.97360 |
| H | -5.97610 | -3.04040 | 9.89660 | | | | |
| C | -3.90380 | -2.76850 | 10.34830 | ---------- | | | |
| C | -5.62300 | -0.95220 | 10.13550 | | | | |
| C | -7.45870 | -1.96910 | 13.63100 | Compound **5.28** | | | |
| C | -8.91980 | -1.51810 | 13.60430 | This structure was assigned as ambiguous. | | | |
| C | -6.61210 | -0.98860 | 14.46850 | B3LYP/6-31g(d) | | | |
| H | -5.57480 | -1.30450 | 14.55410 | SMD implicit solvation in dichloromethane | | | |
| H | -7.02510 | -0.91700 | 15.47470 | was used. | | | |
| H | -6.63590 | 0.00040 | 14.01050 | | | | |
| H | -9.50880 | -2.21920 | 13.01270 | Electronic Energy: -1878.53205755 har- | | | |
| H | -8.99860 | -0.52720 | 13.15680 | tree. | | | |
| H | -9.32270 | -1.48770 | 14.61670 | Free Energy: -1877.803332 hartree. | | | |
| H | -6.68820 | -0.72320 | 10.10530 | | | | |
| H | -5.22050 | -0.75350 | 9.14160 | O | -2.63681 | -0.23670 | 0.48888 |
| H | -5.15430 | -0.25470 | 10.83080 | C | -1.35933 | -0.20129 | 1.14095 |
| O | -3.00890 | -2.00250 | 10.70610 | C | -1.17728 | -1.30427 | 2.17720 |
| O | -3.71580 | -3.98100 | 9.79080 | C | -1.14703 | 1.21930 | 1.75074 |
| C | -2.39540 | -4.49150 | 9.57740 | H | -0.57718 | -0.33271 | 0.38169 |
| C | -2.19820 | -4.70370 | 8.06790 | Si | -3.01118 | -1.03486 | -0.96218 |
| C | -2.18170 | -5.76590 | 10.43760 | H | -0.23653 | 1.15149 | 2.35318 |
| H | -1.64050 | -3.76700 | 9.88780 | C | -2.29864 | 1.65060 | 2.66604 |
| C | -2.05780 | -5.37160 | 11.94390 | C | -2.20693 | -2.04027 | 2.61132 |
| H | -1.22580 | -6.20310 | 10.14380 | C | 0.22024 | -1.51274 | 2.75323 |
| C | -3.24560 | -6.83960 | 10.11180 | C | -4.89281 | -0.75466 | -1.18817 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.01491 | -0.24360 | -2.36030 | C | 0.77714 | 3.93100 | -0.25353 |
| C | -2.59212 | -2.87417 | -0.89192 | C | 1.33197 | 5.34776 | -0.22945 |
| H | -2.06525 | 0.85145 | -2.34492 | C | -0.07571 | 3.52213 | 0.97022 |
| H | -2.37602 | -0.57961 | -3.34078 | H | 0.18842 | 3.78068 | -1.15994 |
| H | -0.95472 | -0.51985 | -2.30215 | C | -0.84310 | 2.21872 | 0.61041 |
| H | -1.54020 | -3.03836 | -0.62918 | H | -0.83905 | 4.30262 | 1.08581 |
| H | -2.75026 | -3.33186 | -1.87723 | C | 0.75465 | 3.47463 | 2.26150 |
| H | -3.20301 | -3.42267 | -0.16647 | H | 0.50912 | 6.06842 | -0.16180 |
| H | -2.07201 | -2.80822 | 3.37042 | H | 1.88674 | 5.55260 | -1.15164 |
| H | -3.21151 | -1.90280 | 2.22505 | H | 2.00628 | 5.51180 | 0.61709 |
| C | 1.22300 | -2.42486 | 1.98445 | O | -2.03603 | 2.63469 | -0.06977 |
| H | 0.08877 | -1.97443 | 3.73825 | H | -0.21686 | 1.66555 | -0.10333 |
| H | 0.70554 | -0.54806 | 2.94291 | H | 1.53315 | 2.70605 | 2.22437 |
| H | 0.67146 | -3.32224 | 1.67151 | H | 0.12378 | 3.27995 | 3.13362 |
| C | 2.30808 | -2.90673 | 2.96631 | H | 1.25045 | 4.43599 | 2.43343 |
| C | 1.78043 | -1.83113 | 0.65931 | H | -2.57177 | 1.82979 | -0.18220 |
| O | 2.80770 | -2.73803 | 0.22060 | H | -2.44526 | 0.92734 | 3.47568 |
| C | 2.32695 | -0.37976 | 0.61366 | H | -3.23908 | 1.73436 | 2.11561 |
| H | 0.95047 | -1.86647 | -0.06316 | H | -2.09280 | 2.62616 | 3.12009 |
| H | 3.07071 | -3.49604 | 2.45185 | C | -5.37492 | -1.54516 | -2.42504 |
| H | 1.85000 | -3.53968 | 3.73594 | H | -6.45065 | -1.38075 | -2.58564 |
| H | 2.80669 | -2.07814 | 3.47894 | H | -4.86110 | -1.23299 | -3.34326 |
| C | 3.45365 | -0.09011 | 1.61505 | H | -5.22529 | -2.62568 | -2.30939 |
| H | 1.49118 | 0.29921 | 0.81571 | C | -5.19865 | 0.74248 | -1.40633 |
| C | 2.75480 | -0.16995 | -0.86119 | H | -4.68530 | 1.14635 | -2.28781 |
| O | 3.78869 | -1.10857 | -1.17357 | H | -6.27756 | 0.89246 | -1.56136 |
| C | 3.25030 | 1.25015 | -1.24769 | H | -4.91112 | 1.35169 | -0.54056 |
| H | 1.88547 | -0.37141 | -1.50330 | C | -5.66551 | -1.24488 | 0.05449 |
| H | 3.08208 | -0.11648 | 2.64336 | H | -5.50659 | -2.31364 | 0.24610 |
| H | 3.88128 | 0.90580 | 1.45882 | H | -5.37409 | -0.69436 | 0.95645 |
| H | 4.26322 | -0.81954 | 1.52595 | H | -6.74697 | -1.09834 | -0.08648 |
| H | 3.91070 | 1.64386 | -0.47162 | ---------- | | | |
| C | 2.03007 | 2.16324 | -1.35966 | | | | |
| C | 3.99413 | 1.25254 | -2.59366 | Compound **5.28** | | | |
| C | 3.39613 | -2.47971 | -1.05450 | This structure was assigned as ambiguous. | | | |
| C | 4.69149 | -3.28145 | -1.08390 | B3LYP/6-31g(d) | | | |
| C | 2.45849 | -2.89825 | -2.19685 | Gas phase. | | | |
| H | 1.50663 | -2.36116 | -2.18656 | | | | |
| H | 2.24091 | -3.96819 | -2.11776 | Electronic Energy: -1878.50549055 hartree. | | | |
| H | 2.94189 | -2.71080 | -3.16106 | | | | |
| H | 5.34755 | -2.95763 | -0.27046 | Free Energy: -1877.775902 hartree. | | | |
| H | 5.20892 | -3.13237 | -2.03666 | | | | |
| H | 4.47860 | -4.34793 | -0.96328 | O | -2.59460 | -0.32193 | 0.49417 |
| H | 4.89677 | 0.64159 | -2.52905 | C | -1.32307 | -0.26056 | 1.15000 |
| H | 4.28456 | 2.27373 | -2.86556 | C | -1.10823 | -1.38829 | 2.15213 |
| H | 3.36028 | 0.85564 | -3.39279 | C | -1.16006 | 1.15171 | 1.78950 |
| O | 1.23780 | 2.10673 | -2.28309 | H | -0.53423 | -0.34547 | 0.38829 |
| O | 1.93086 | 3.01794 | -0.32454 | Si | -2.90755 | -1.03862 | -1.01286 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.21606 | 1.12221 | 2.34309 | H | 4.72044 | 0.76939 | -2.64769 |
| C | -2.28461 | 1.48836 | 2.77700 | H | 4.08489 | 2.40478 | -2.93574 |
| C | -2.10720 | -2.19278 | 2.52875 | H | 3.14325 | 0.99039 | -3.43795 |
| C | 0.28378 | -1.54608 | 2.75617 | O | 1.00846 | 2.03972 | -2.22106 |
| C | -4.81299 | -0.94644 | -1.17282 | O | 1.76419 | 3.07760 | -0.34780 |
| C | -2.04489 | -0.03495 | -2.36168 | C | 0.57379 | 3.93832 | -0.25739 |
| C | -2.27752 | -2.81929 | -1.06730 | C | 1.07061 | 5.37827 | -0.26166 |
| H | -2.30568 | 1.02823 | -2.31608 | C | -0.23273 | 3.51553 | 0.99251 |
| H | -2.31094 | -0.40506 | -3.35932 | H | -0.03219 | 3.75023 | -1.14577 |
| H | -0.95288 | -0.08775 | -2.28017 | C | -0.98327 | 2.19375 | 0.65860 |
| H | -1.19621 | -2.86131 | -0.89034 | H | -1.01653 | 4.27242 | 1.12439 |
| H | -2.46268 | -3.26255 | -2.05343 | C | 0.63569 | 3.49997 | 2.25997 |
| H | -2.75460 | -3.45361 | -0.31353 | H | 0.22201 | 6.06546 | -0.17300 |
| H | -1.95216 | -2.97970 | 3.26317 | H | 1.59028 | 5.59783 | -1.19991 |
| H | -3.10495 | -2.09063 | 2.11730 | H | 1.76312 | 5.57377 | 0.56285 |
| C | 1.34005 | -2.39949 | 1.99446 | O | -2.23606 | 2.58811 | 0.09450 |
| H | 0.15385 | -2.02975 | 3.73097 | H | -0.39851 | 1.68661 | -0.12144 |
| H | 0.72235 | -0.56491 | 2.97672 | H | 1.44197 | 2.76293 | 2.19566 |
| H | 0.84151 | -3.32885 | 1.68647 | H | 0.03786 | 3.27949 | 3.14899 |
| C | 2.45716 | -2.81110 | 2.97281 | H | 1.10103 | 4.47812 | 2.41976 |
| C | 1.85749 | -1.78538 | 0.66334 | H | -2.73726 | 1.76488 | -0.03455 |
| O | 2.92375 | -2.63887 | 0.22490 | H | -2.33080 | 0.74722 | 3.58119 |
| C | 2.32893 | -0.30837 | 0.60038 | H | -3.25685 | 1.50784 | 2.27979 |
| H | 1.02249 | -1.86733 | -0.05235 | H | -2.12561 | 2.47360 | 3.22792 |
| H | 3.24768 | -3.35557 | 2.45322 | C | -5.25013 | -1.55660 | -2.52318 |
| H | 2.04144 | -3.46373 | 3.74940 | H | -6.34381 | -1.50774 | -2.62547 |
| H | 2.90986 | -1.95156 | 3.47660 | H | -4.82114 | -1.01890 | -3.37766 |
| C | 3.45693 | 0.04698 | 1.57909 | H | -4.96359 | -2.61183 | -2.61224 |
| H | 1.46727 | 0.33459 | 0.81072 | C | -5.27963 | 0.52432 | -1.11183 |
| C | 2.72364 | -0.09252 | -0.88282 | H | -4.84622 | 1.12956 | -1.91714 |
| O | 3.80284 | -0.97330 | -1.19655 | H | -6.37302 | 0.58246 | -1.21438 |
| C | 3.12750 | 1.34807 | -1.28999 | H | -5.01813 | 0.99381 | -0.15614 |
| H | 1.85623 | -0.34609 | -1.51051 | C | -5.48451 | -1.72868 | -0.02385 |
| H | 3.11185 | -0.01049 | 2.61497 | H | -5.20561 | -2.78962 | -0.02934 |
| H | 3.81143 | 1.07013 | 1.41953 | H | -5.21706 | -1.31384 | 0.95443 |
| H | 4.30731 | -0.62930 | 1.46376 | H | -6.57921 | -1.67937 | -0.11719 |
| H | 3.79611 | 1.77886 | -0.54084 | --- | | | |
| C | 1.85102 | 2.18663 | -1.35724 | | | | |
| C | 3.81474 | 1.37786 | -2.66622 | Compound **5.28** | | | |
| C | 3.49374 | -2.36117 | -1.05385 | This structure was assigned as ambiguous. | | | |
| C | 4.83504 | -3.08410 | -1.07401 | M06-2X/6-31g(d) | | | |
| C | 2.57663 | -2.85241 | -2.18535 | SMD implicit solvation in dichloromethane | | | |
| H | 1.59384 | -2.37422 | -2.17400 | was used. | | | |
| H | 2.42445 | -3.93151 | -2.08802 | | | | |
| H | 3.04066 | -2.64618 | -3.15454 | Electronic Energy: -1877.81620115 har- | | | |
| H | 5.46824 | -2.69943 | -0.27038 | tree. | | | |
| H | 5.33796 | -2.92035 | -2.03146 | Free Energy: -1877.076409 hartree. | | | |
| H | 4.68620 | -4.15754 | -0.92711 | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O | -2.56163 | -0.22198 | 0.59432 | H | 1.06441 | -2.39205 | -1.92204 |
| C | -1.30047 | -0.15799 | 1.24924 | H | 1.83374 | -3.98175 | -1.95693 |
| C | -1.13057 | -1.22699 | 2.30814 | H | 2.37413 | -2.70602 | -3.07339 |
| C | -1.09792 | 1.26745 | 1.80314 | H | 5.09294 | -2.98705 | -0.48033 |
| H | -0.50901 | -0.31145 | 0.50010 | H | 4.74435 | -3.23000 | -2.21048 |
| Si | -2.70678 | -1.04790 | -0.87371 | H | 4.11432 | -4.37987 | -1.00523 |
| H | -0.17367 | 1.24093 | 2.38794 | H | 4.50985 | 0.48725 | -2.78393 |
| C | -2.24541 | 1.70942 | 2.70586 | H | 3.85032 | 2.08817 | -3.17837 |
| C | -2.15278 | -1.98990 | 2.69746 | H | 2.88424 | 0.63209 | -3.48216 |
| C | 0.25427 | -1.38622 | 2.90782 | O | 0.94308 | 2.02611 | -2.29128 |
| C | -4.53838 | -0.87717 | -1.30265 | O | 1.79507 | 3.01486 | -0.45002 |
| C | -1.59365 | -0.18873 | -2.11902 | C | 0.66923 | 3.93039 | -0.33364 |
| C | -2.18201 | -2.84150 | -0.70640 | C | 1.24042 | 5.33534 | -0.33339 |
| H | -1.68266 | 0.90263 | -2.06779 | C | -0.11316 | 3.53592 | 0.92953 |
| H | -1.82767 | -0.49957 | -3.14434 | H | 0.02594 | 3.78413 | -1.20482 |
| H | -0.53847 | -0.43277 | -1.94238 | C | -0.85423 | 2.21842 | 0.62258 |
| H | -1.20888 | -2.92866 | -0.20810 | H | -0.88414 | 4.30221 | 1.08129 |
| H | -2.08267 | -3.29600 | -1.69983 | C | 0.79222 | 3.49957 | 2.16111 |
| H | -2.89769 | -3.43762 | -0.12990 | H | 0.43731 | 6.06400 | -0.18688 |
| H | -2.02884 | -2.74676 | 3.46861 | H | 1.72424 | 5.54477 | -1.29193 |
| H | -3.13873 | -1.88054 | 2.25434 | H | 1.98196 | 5.46731 | 0.45937 |
| C | 1.24119 | -2.29405 | 2.14324 | O | -2.06773 | 2.57948 | -0.02730 |
| H | 0.13654 | -1.82230 | 3.90614 | H | -0.23302 | 1.65439 | -0.09186 |
| H | 0.73252 | -0.40930 | 3.05742 | H | 1.56589 | 2.72898 | 2.07104 |
| H | 0.71541 | -3.23293 | 1.91883 | H | 0.21716 | 3.30302 | 3.07038 |
| C | 2.41060 | -2.65379 | 3.06849 | H | 1.29431 | 4.46211 | 2.29690 |
| C | 1.66642 | -1.76207 | 0.75823 | H | -2.58734 | 1.76066 | -0.09768 |
| O | 2.64704 | -2.68189 | 0.28134 | H | -2.33548 | 1.04884 | 3.57406 |
| C | 2.20839 | -0.32147 | 0.60444 | H | -3.19616 | 1.69325 | 2.16633 |
| H | 0.77637 | -1.83089 | 0.11219 | H | -2.08325 | 2.73035 | 3.06788 |
| H | 3.20158 | -3.17245 | 2.52276 | C | -4.84610 | -1.68430 | -2.57108 |
| H | 2.05201 | -3.31651 | 3.86326 | H | -5.90987 | -1.59068 | -2.83087 |
| H | 2.84276 | -1.77258 | 3.55076 | H | -4.26626 | -1.33371 | -3.43363 |
| C | 3.41958 | -0.02885 | 1.48765 | H | -4.63480 | -2.75202 | -2.43414 |
| H | 1.40999 | 0.39156 | 0.84857 | C | -4.88279 | 0.59998 | -1.53632 |
| C | 2.51774 | -0.18473 | -0.90077 | H | -4.29000 | 1.04037 | -2.34752 |
| O | 3.50190 | -1.14576 | -1.24939 | H | -5.94277 | 0.70474 | -1.80795 |
| C | 3.00813 | 1.19248 | -1.39016 | H | -4.72250 | 1.19862 | -0.63042 |
| H | 1.59513 | -0.39214 | -1.46690 | C | -5.38885 | -1.40997 | -0.14168 |
| H | 3.12610 | 0.02883 | 2.53905 | H | -5.18647 | -2.46869 | 0.06080 |
| H | 3.88010 | 0.93022 | 1.23202 | H | -5.20486 | -0.84702 | 0.78060 |
| H | 4.17826 | -0.81006 | 1.38300 | H | -6.45776 | -1.31998 | -0.38209 |
| H | 3.74566 | 1.60817 | -0.70013 | ---------- | | | |
| C | 1.80269 | 2.11671 | -1.44234 | | | | |
| C | 3.60274 | 1.09269 | -2.79738 | Compound **5.28** | | | |
| C | 3.08942 | -2.48851 | -1.04981 | This structure was assigned as incorrect. | | | |
| C | 4.34288 | -3.32891 | -1.19849 | B3LYP/6-31g(d) | | | |
| C | 2.01851 | -2.90859 | -2.05893 | Gas phase. | | | |

Electronic Energy: -1878.50957688 hartree.
Free Energy: -1877.781281 hartree.

| | | | |
|---|---|---|---|
| O | 3.27090 | 0.11863 | -0.07800 |
| C | 2.07406 | 0.57354 | 0.57053 |
| C | 1.09897 | -0.59372 | 0.74816 |
| C | 1.52575 | 1.76780 | -0.25656 |
| H | 2.31824 | 0.95623 | 1.56949 |
| Si | 4.55538 | -0.70970 | 0.63588 |
| H | 1.33287 | 1.39505 | -1.26921 |
| C | 2.58110 | 2.88023 | -0.35751 |
| C | 0.73308 | -0.93946 | 1.98842 |
| C | 0.69229 | -1.32976 | -0.51663 |
| C | 6.01786 | -0.48244 | -0.58114 |
| C | 4.93467 | 0.03171 | 2.33527 |
| C | 4.14343 | -2.54294 | 0.84786 |
| H | 5.84294 | -0.41385 | 2.75926 |
| H | 5.08839 | 1.11564 | 2.28693 |
| H | 4.12193 | -0.15773 | 3.04639 |
| H | 3.23259 | -2.66385 | 1.44407 |
| H | 4.95212 | -3.07482 | 1.36346 |
| H | 3.97950 | -3.04032 | -0.11508 |
| H | 0.07950 | -1.78012 | 2.19818 |
| H | 1.08110 | -0.37963 | 2.85282 |
| C | -0.34195 | -2.47674 | -0.43818 |
| H | 1.61278 | -1.74050 | -0.95284 |
| H | 0.35028 | -0.59619 | -1.25953 |
| H | -0.01841 | -3.17022 | 0.35105 |
| C | -0.31549 | -3.28517 | -1.74927 |
| C | -1.75906 | -2.01245 | -0.00358 |
| O | -2.65722 | -3.10963 | -0.22442 |
| C | -2.36290 | -0.72886 | -0.61494 |
| H | -1.69986 | -1.82058 | 1.07635 |
| H | -1.08157 | -4.06297 | -1.74062 |
| H | 0.66336 | -3.76505 | -1.86577 |
| H | -0.47941 | -2.65748 | -2.63084 |
| C | -2.53261 | -0.76097 | -2.13980 |
| H | -1.71209 | 0.10585 | -0.34500 |
| C | -3.70066 | -0.54198 | 0.13734 |
| O | -4.53291 | -1.67288 | -0.13425 |
| C | -4.51273 | 0.73986 | -0.18569 |
| H | -3.48362 | -0.50180 | 1.21713 |
| H | -1.56297 | -0.79790 | -2.64418 |
| H | -3.04285 | 0.13784 | -2.49952 |
| H | -3.11250 | -1.63202 | -2.45431 |
| H | -4.56298 | 0.86829 | -1.27122 |
| C | -3.77566 | 1.94421 | 0.40415 |
| C | -5.93428 | 0.67288 | 0.38818 |
| C | -3.98640 | -2.93455 | 0.26419 |
| C | -4.83034 | -3.98629 | -0.44577 |
| C | -4.04439 | -3.10751 | 1.79067 |
| H | -3.43798 | -2.37102 | 2.32417 |
| H | -3.67807 | -4.10290 | 2.05942 |
| H | -5.07799 | -3.00577 | 2.13485 |
| H | -4.77343 | -3.82978 | -1.52607 |
| H | -5.87457 | -3.90899 | -0.12974 |
| H | -4.45835 | -4.98778 | -0.21148 |
| H | -6.46863 | -0.17953 | -0.03436 |
| H | -6.48440 | 1.59004 | 0.15378 |
| H | -5.90845 | 0.57124 | 1.47695 |
| O | -4.01739 | 2.42722 | 1.48991 |
| O | -2.80066 | 2.39715 | -0.42009 |
| C | -1.99073 | 3.52315 | 0.04766 |
| C | -2.67738 | 4.82315 | -0.35917 |
| C | -0.56973 | 3.32987 | -0.52582 |
| H | -1.94392 | 3.46407 | 1.13664 |
| C | 0.18746 | 2.27525 | 0.32773 |
| H | -0.05692 | 4.29280 | -0.37446 |
| C | -0.58057 | 3.03456 | -2.03509 |
| H | -2.08657 | 5.68274 | -0.02251 |
| H | -3.66302 | 4.88593 | 0.11094 |
| H | -2.80489 | 4.89497 | -1.44425 |
| O | 0.35441 | 2.75618 | 1.66868 |
| H | -0.47041 | 1.41200 | 0.45202 |
| H | -0.97472 | 2.03586 | -2.24537 |
| H | 0.42332 | 3.10399 | -2.46393 |
| H | -1.21162 | 3.75305 | -2.56822 |
| H | 0.91243 | 3.54941 | 1.62563 |
| H | 2.22217 | 3.72598 | -0.95494 |
| H | 2.86137 | 3.26062 | 0.63384 |
| H | 3.49029 | 2.49897 | -0.82565 |
| C | 7.21350 | -1.35041 | -0.12925 |
| H | 8.06204 | -1.21607 | -0.81571 |
| H | 7.56555 | -1.07948 | 0.87444 |
| H | 6.96890 | -2.41927 | -0.12147 |
| C | 6.46490 | 0.99405 | -0.62180 |
| H | 6.81120 | 1.34507 | 0.35801 |
| H | 7.29908 | 1.12152 | -1.32728 |
| H | 5.65480 | 1.65582 | -0.94829 |
| C | 5.58753 | -0.91495 | -1.99946 |
| H | 5.28778 | -1.96977 | -2.03271 |
| H | 4.74492 | -0.31717 | -2.36342 |
| H | 6.42005 | -0.79043 | -2.70748 |

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Compound **5.28**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1878.53740493 hartree.
Free Energy: -1877.811310 hartree.

| | | | |
|---|---|---|---|
| O | -3.25738 | 0.04100 | 0.05613 |
| C | -2.05895 | 0.52056 | -0.58147 |
| C | -1.08178 | -0.64712 | -0.74826 |
| C | -1.52873 | 1.72039 | 0.25095 |
| H | -2.29531 | 0.89829 | -1.58383 |
| Si | -4.67576 | -0.43530 | -0.72330 |
| H | -1.35616 | 1.35278 | 1.26902 |
| C | -2.58351 | 2.83561 | 0.32289 |
| C | -0.72603 | -1.01262 | -1.98630 |
| C | -0.66244 | -1.36676 | 0.52264 |
| C | -5.91592 | -0.78315 | 0.69624 |
| C | -5.29383 | 0.94787 | -1.85514 |
| C | -4.39120 | -1.97952 | -1.77655 |
| H | -5.60460 | 1.84026 | -1.29904 |
| H | -6.15400 | 0.60911 | -2.44676 |
| H | -4.51888 | 1.25575 | -2.56865 |
| H | -3.89734 | -2.78091 | -1.21456 |
| H | -3.76366 | -1.75505 | -2.64751 |
| H | -5.34225 | -2.37608 | -2.15598 |
| H | -0.07471 | -1.85717 | -2.19084 |
| H | -1.08822 | -0.47199 | -2.85813 |
| C | 0.38518 | -2.50258 | 0.44827 |
| H | -1.57576 | -1.78882 | 0.96354 |
| H | -0.32547 | -0.62389 | 1.25758 |
| H | 0.07111 | -3.20190 | -0.33939 |
| C | 0.36645 | -3.30389 | 1.76304 |
| C | 1.79156 | -2.01646 | 0.00847 |
| O | 2.70722 | -3.11302 | 0.18601 |
| C | 2.39709 | -0.74704 | 0.64609 |
| H | 1.71504 | -1.79915 | -1.06372 |
| H | 1.14898 | -4.06708 | 1.76849 |
| H | -0.60103 | -3.80850 | 1.87418 |
| H | 0.50539 | -2.66836 | 2.64367 |
| C | 2.59551 | -0.82236 | 2.16590 |
| H | 1.73451 | 0.08948 | 0.41419 |
| C | 3.71399 | -0.52727 | -0.13133 |
| O | 4.56736 | -1.65545 | 0.09453 |
| C | 4.51097 | 0.76353 | 0.19799 |
| H | 3.47042 | -0.46986 | -1.20295 |
| H | 3.15020 | 0.04418 | 2.54038 |
| H | 3.14653 | -1.72191 | 2.45365 |
| H | 1.63451 | -0.83322 | 2.68790 |
| H | 4.56923 | 0.89240 | 1.28265 |
| C | 3.74463 | 1.95259 | -0.38366 |
| C | 5.92891 | 0.72519 | -0.38672 |
| C | 4.02300 | -2.91197 | -0.33246 |
| C | 4.89554 | -3.97721 | 0.31957 |
| C | 4.04583 | -3.03668 | -1.86347 |
| H | 3.41976 | -2.29196 | -2.36192 |
| H | 3.68593 | -4.02871 | -2.15527 |
| H | 5.07079 | -2.91623 | -2.22887 |
| H | 4.86839 | -3.86517 | 1.40758 |
| H | 5.93111 | -3.87968 | -0.02059 |
| H | 4.53279 | -4.97579 | 0.05733 |
| H | 6.49767 | -0.09470 | 0.05713 |
| H | 6.45428 | 1.66417 | -0.18078 |
| H | 5.90521 | 0.58379 | -1.47190 |
| O | 3.94291 | 2.40977 | -1.49378 |
| O | 2.80563 | 2.41962 | 0.46363 |
| C | 1.96614 | 3.53760 | 0.01384 |
| C | 2.62020 | 4.83995 | 0.45952 |
| C | 0.54237 | 3.30148 | 0.56227 |
| H | 1.93328 | 3.50142 | -1.07587 |
| C | -0.17587 | 2.22753 | -0.30121 |
| H | 0.00906 | 4.25070 | 0.40145 |
| C | 0.53216 | 3.00529 | 2.07055 |
| H | 2.01661 | 5.69337 | 0.12983 |
| H | 3.61437 | 4.93755 | 0.01095 |
| H | 2.72761 | 4.89337 | 1.54784 |
| O | -0.30637 | 2.69100 | -1.65504 |
| H | 0.49085 | 1.36659 | -0.39174 |
| H | 0.94590 | 2.01651 | 2.29281 |
| H | -0.48247 | 3.04833 | 2.47710 |
| H | 1.13107 | 3.74183 | 2.61709 |
| H | -0.84777 | 3.49951 | -1.63418 |
| H | -3.50364 | 2.46682 | 0.78194 |
| H | -2.84228 | 3.21409 | -0.67451 |
| H | -2.23049 | 3.68290 | 0.92131 |
| C | -5.46599 | -2.01136 | 1.51487 |
| H | -6.17631 | -2.20800 | 2.33209 |
| H | -5.41685 | -2.91983 | 0.90182 |
| H | -4.47906 | -1.86088 | 1.96921 |
| C | -7.31200 | -1.06273 | 0.09878 |
| H | -7.30712 | -1.92232 | -0.58337 |
| H | -8.03207 | -1.28915 | 0.89919 |

| | | | |
|---|---|---|---|
| H | -7.70284 | -0.20012 | -0.45517 |
| C | -6.00726 | 0.43720 | 1.63567 |
| H | -5.04194 | 0.65946 | 2.10445 |
| H | -6.33923 | 1.33994 | 1.10715 |
| H | -6.73169 | 0.24837 | 2.44255 |

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Compound **5.28**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1877.81663037 hartree.
Free Energy: -1877.081012 hartree.

| | | | |
|---|---|---|---|
| O | -3.23596 | 0.08084 | 0.13645 |
| C | -2.06843 | 0.57400 | -0.51738 |
| C | -1.09309 | -0.57941 | -0.71764 |
| C | -1.51346 | 1.73258 | 0.32925 |
| H | -2.32303 | 0.97836 | -1.50945 |
| Si | -4.64315 | -0.28121 | -0.70338 |
| H | -1.31568 | 1.33081 | 1.32985 |
| C | -2.55322 | 2.84548 | 0.45678 |
| C | -0.74294 | -0.93093 | -1.95621 |
| C | -0.65604 | -1.28756 | 0.54468 |
| C | -5.81991 | -0.96212 | 0.61232 |
| C | -5.32925 | 1.27713 | -1.49883 |
| C | -4.30813 | -1.55106 | -2.04752 |
| H | -5.65144 | 2.01580 | -0.75631 |
| H | -4.58106 | 1.75433 | -2.14299 |
| H | -6.19199 | 1.03802 | -2.13209 |
| H | -3.72997 | -1.11635 | -2.87108 |
| H | -5.25073 | -1.91865 | -2.47190 |
| H | -3.75029 | -2.41325 | -1.66616 |
| H | -0.09058 | -1.77284 | -2.16868 |
| H | -1.11728 | -0.38211 | -2.81770 |
| C | 0.33777 | -2.45358 | 0.43327 |
| H | -1.56741 | -1.65832 | 1.03390 |
| H | -0.24804 | -0.54258 | 1.24335 |
| H | -0.02951 | -3.14259 | -0.34045 |
| C | 0.34762 | -3.24056 | 1.74949 |
| C | 1.73884 | -2.01136 | -0.04191 |
| O | 2.63440 | -3.09498 | 0.20197 |
| C | 2.33678 | -0.72020 | 0.53716 |
| H | 1.67152 | -1.84758 | -1.12574 |
| H | 1.09758 | -4.03373 | 1.72751 |
| H | -0.63447 | -3.69932 | 1.90645 |
| H | 0.55242 | -2.60093 | 2.61302 |
| C | 2.50384 | -0.73320 | 2.05453 |
| H | 1.68599 | 0.10770 | 0.24649 |
| C | 3.67429 | -0.55106 | -0.20024 |
| O | 4.49447 | -1.67687 | 0.08574 |
| C | 4.49962 | 0.70690 | 0.13222 |
| H | 3.46945 | -0.50952 | -1.28313 |
| H | 1.53428 | -0.74776 | 2.55930 |
| H | 3.02942 | 0.16152 | 2.40176 |
| H | 3.07028 | -1.61266 | 2.37574 |
| H | 4.59723 | 0.80344 | 1.21778 |
| C | 3.75222 | 1.92524 | -0.38631 |
| C | 5.88193 | 0.63837 | -0.51168 |
| C | 3.94481 | -2.92706 | -0.30976 |
| C | 4.79594 | -3.98106 | 0.37184 |
| C | 3.97675 | -3.08978 | -1.82997 |
| H | 3.34248 | -2.36964 | -2.35189 |
| H | 3.63427 | -4.09490 | -2.09185 |
| H | 5.00278 | -2.96213 | -2.18681 |
| H | 4.76529 | -3.82739 | 1.45384 |
| H | 5.83117 | -3.90838 | 0.02818 |
| H | 4.41247 | -4.97825 | 0.14071 |
| H | 6.45772 | -0.17993 | -0.07706 |
| H | 6.42570 | 1.57435 | -0.35581 |
| H | 5.79720 | 0.47098 | -1.58989 |
| O | 4.00204 | 2.47764 | -1.43376 |
| O | 2.76849 | 2.31093 | 0.43936 |
| C | 1.97443 | 3.45817 | 0.03821 |
| C | 2.67232 | 4.72255 | 0.50662 |
| C | 0.57017 | 3.25119 | 0.61936 |
| H | 1.90903 | 3.45427 | -1.05269 |
| C | -0.19129 | 2.24262 | -0.26036 |
| H | 0.05875 | 4.22165 | 0.53305 |
| C | 0.61037 | 2.84279 | 2.09290 |
| H | 2.09140 | 5.60078 | 0.20865 |
| H | 3.66343 | 4.79809 | 0.05022 |
| H | 2.78868 | 4.73416 | 1.59449 |
| O | -0.38620 | 2.76764 | -1.57034 |
| H | 0.46559 | 1.38040 | -0.41765 |
| H | 0.93660 | 1.80173 | 2.20175 |
| H | -0.37424 | 2.94272 | 2.55847 |
| H | 1.30740 | 3.46895 | 2.65864 |
| H | -0.90023 | 3.58735 | -1.48110 |
| H | -2.17931 | 3.67416 | 1.06846 |
| H | -2.83146 | 3.24598 | -0.52624 |
| H | -3.46398 | 2.46552 | 0.92656 |
| C | -7.24004 | -1.05100 | 0.03705 |

| | | | |
|---|---|---|---|
| H | -7.92357 | -1.49078 | 0.77696 |
| H | -7.63370 | -0.06211 | -0.22721 |
| H | -7.28320 | -1.68022 | -0.86102 |
| C | -5.82683 | -0.03325 | 1.83344 |
| H | -6.13915 | 0.98487 | 1.56926 |
| H | -6.53096 | -0.40653 | 2.59078 |
| H | -4.83596 | 0.02869 | 2.29617 |
| C | -5.35835 | -2.36060 | 1.04291 |
| H | -5.39518 | -3.07418 | 0.21089 |
| H | -4.33169 | -2.34737 | 1.42896 |
| H | -6.00807 | -2.74848 | 1.84039 |

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Compound **5.29**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -92.563553 kJ.

| | | | |
|---|---|---|---|
| C | -2.18580 | 13.55050 | -7.31660 |
| C | -2.31580 | 12.39650 | -6.28660 |
| C | -1.20850 | 13.27190 | -8.48270 |
| H | -0.26410 | 12.92200 | -8.07180 |
| C | -0.90110 | 14.56410 | -9.26680 |
| C | -1.02610 | 11.87510 | -5.62930 |
| C | -1.17530 | 10.63700 | -4.70410 |
| H | -0.60970 | 12.70240 | -5.05510 |
| H | -0.29740 | 11.64490 | -6.40250 |
| H | -1.90790 | 10.90410 | -3.94010 |
| C | 0.13260 | 10.39020 | -3.92380 |
| C | -1.74070 | 9.35710 | -5.39370 |
| O | -1.51620 | 8.21320 | -4.57480 |
| C | -1.25060 | 9.01430 | -6.81810 |
| H | -2.81810 | 9.50980 | -5.44860 |
| H | 0.96000 | 10.09940 | -4.56640 |
| H | 0.00640 | 9.60230 | -3.18050 |
| H | 0.43900 | 11.28540 | -3.38270 |
| C | 0.26560 | 8.75220 | -6.92260 |
| H | -1.47780 | 9.85190 | -7.45870 |
| C | -2.10260 | 7.81560 | -7.28550 |
| O | -1.80290 | 6.75010 | -6.38630 |
| C | -1.90940 | 7.35570 | -8.75530 |
| H | -3.15820 | 8.07220 | -7.18910 |
| H | 0.55410 | 8.44140 | -7.92510 |
| H | 0.58280 | 7.97190 | -6.23020 |
| H | 0.84140 | 9.64920 | -6.70760 |
| H | -0.85350 | 7.16470 | -8.93880 |
| C | -2.36580 | 8.43400 | -9.75600 |
| C | -2.66050 | 6.03590 | -9.02190 |
| C | -2.04970 | 7.00010 | -5.02910 |
| C | -1.31210 | 5.90280 | -4.26030 |
| C | -3.56100 | 6.93410 | -4.73150 |
| H | -4.11660 | 7.71680 | -5.24330 |
| H | -3.72850 | 7.04600 | -3.66020 |
| H | -3.95610 | 5.96890 | -5.04830 |
| H | -1.46120 | 6.03040 | -3.18800 |
| H | -0.24500 | 5.95840 | -4.47590 |
| H | -1.68120 | 4.92180 | -4.55960 |
| H | -3.71690 | 6.12080 | -8.76410 |
| H | -2.24090 | 5.22190 | -8.43090 |
| H | -2.59560 | 5.74510 | -10.07080 |
| O | -3.53940 | 8.52370 | -10.11660 |
| O | -1.36520 | 9.24580 | -10.15550 |
| C | -1.60490 | 10.31250 | -11.07880 |
| C | -1.07940 | 9.89370 | -12.46140 |
| C | -0.97280 | 11.62240 | -10.53760 |
| H | -2.67560 | 10.49460 | -11.18630 |
| C | -1.83040 | 12.16980 | -9.36910 |
| H | -1.00560 | 12.36680 | -11.33430 |
| C | 0.51180 | 11.41320 | -10.16010 |
| H | -1.62640 | 9.02620 | -12.83140 |
| H | -0.02360 | 9.62660 | -12.43680 |
| H | -1.20930 | 10.69520 | -13.18870 |
| O | -3.05750 | 12.69500 | -9.85160 |
| H | -2.08120 | 11.31700 | -8.75160 |
| H | 1.07760 | 10.97730 | -10.98210 |
| H | 0.61650 | 10.74970 | -9.30140 |
| H | 1.00520 | 12.35270 | -9.91610 |
| H | -1.80660 | 14.98980 | -9.70130 |
| H | -0.20120 | 14.38730 | -10.08240 |
| H | -0.46360 | 15.32210 | -8.61740 |
| H | -1.83900 | 14.41990 | -6.75810 |
| O | -3.44760 | 13.89190 | -7.90550 |
| C | -3.96420 | 12.96860 | -8.82460 |
| H | -4.25500 | 12.03780 | -8.33270 |
| O | -3.41240 | 11.92720 | -5.98420 |
| C | -5.19150 | 13.61000 | -9.46600 |
| H | -5.62880 | 12.92540 | -10.19280 |
| H | -5.93250 | 13.83580 | -8.69910 |
| H | -4.90690 | 14.53320 | -9.97070 |

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Compound **5.29**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -79.786934 kJ.

| | | | |
|---|---|---|---|
| C | -1.92140 | 13.50440 | -7.41410 |
| C | -1.32850 | 12.53440 | -6.36100 |
| C | -1.22370 | 13.44180 | -8.80010 |
| H | -0.14480 | 13.44590 | -8.64360 |
| C | -1.56310 | 14.67530 | -9.65790 |
| C | -2.23530 | 12.01590 | -5.22630 |
| C | -1.85790 | 10.67630 | -4.51730 |
| H | -3.25660 | 11.94070 | -5.59550 |
| H | -2.25930 | 12.80590 | -4.47630 |
| H | -2.58040 | 10.62200 | -3.70170 |
| C | -0.51170 | 10.69080 | -3.76160 |
| C | -2.16730 | 9.37960 | -5.32400 |
| O | -1.94850 | 8.22100 | -4.52440 |
| C | -1.47640 | 9.12980 | -6.67750 |
| H | -3.23850 | 9.44510 | -5.51720 |
| H | 0.35340 | 10.82360 | -4.40410 |
| H | -0.36370 | 9.76230 | -3.20950 |
| H | -0.48890 | 11.50250 | -3.03490 |
| C | 0.05260 | 8.92040 | -6.59810 |
| H | -1.67440 | 9.98250 | -7.30280 |
| C | -2.19040 | 7.91290 | -7.29700 |
| O | -1.91470 | 6.82070 | -6.42220 |
| C | -1.80970 | 7.59760 | -8.77000 |
| H | -3.26710 | 8.08550 | -7.29430 |
| H | 0.48170 | 8.68690 | -7.57010 |
| H | 0.31230 | 8.10800 | -5.91950 |
| H | 0.57380 | 9.80840 | -6.25850 |
| H | -0.72780 | 7.52840 | -8.86520 |
| C | -2.30330 | 8.71000 | -9.71210 |
| C | -2.39530 | 6.24800 | -9.22270 |
| C | -2.31800 | 6.98740 | -5.08630 |
| C | -1.56930 | 5.92030 | -4.28630 |
| C | -3.83970 | 6.77990 | -4.95560 |
| H | -4.40550 | 7.53660 | -5.49440 |
| H | -4.12670 | 6.82490 | -3.90490 |
| H | -4.11180 | 5.80090 | -5.35050 |
| H | -1.83880 | 5.98260 | -3.23190 |
| H | -0.49480 | 6.07630 | -4.38380 |
| H | -1.81590 | 4.92710 | -4.66190 |
| H | -3.47870 | 6.22430 | -9.09980 |
| H | -1.97790 | 5.42820 | -8.63800 |
| H | -2.17220 | 6.04960 | -10.27140 |
| O | -3.49680 | 9.01090 | -9.75720 |
| O | -1.31580 | 9.30260 | -10.42640 |
| C | -1.61250 | 10.37720 | -11.32740 |
| C | -1.14250 | 9.96310 | -12.73060 |
| C | -1.02040 | 11.73030 | -10.83160 |
| H | -2.69190 | 10.51560 | -11.40600 |
| C | -1.63950 | 12.11410 | -9.46790 |
| H | -1.30770 | 12.49330 | -11.55540 |
| C | 0.52030 | 11.69670 | -10.76610 |
| H | -1.69640 | 9.09000 | -13.07630 |
| H | -0.08470 | 9.70240 | -12.74680 |
| H | -1.30760 | 10.76330 | -13.45210 |
| O | -3.05480 | 12.16130 | -9.57460 |
| H | -1.34770 | 11.31080 | -8.80640 |
| H | 0.96160 | 11.45420 | -11.73170 |
| H | 0.86950 | 10.95710 | -10.04460 |
| H | 0.93080 | 12.66300 | -10.47670 |
| H | -2.63160 | 14.72990 | -9.86980 |
| H | -1.03510 | 14.65590 | -10.61070 |
| H | -1.28130 | 15.59590 | -9.14720 |
| H | -1.78230 | 14.50270 | -6.99960 |
| O | -3.32940 | 13.31610 | -7.59270 |
| C | -3.69140 | 12.18930 | -8.33830 |
| H | -3.47390 | 11.26890 | -7.79560 |
| O | -0.14380 | 12.21620 | -6.42560 |
| C | -5.19080 | 12.27990 | -8.60310 |
| H | -5.51280 | 11.41540 | -9.18470 |
| H | -5.73530 | 12.29720 | -7.65920 |
| H | -5.41460 | 13.18830 | -9.16260 |

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Compound **5.29**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1465.22289144 hartree.
Free Energy: -1464.656251 hartree.

| | | | |
|---|---|---|---|
| C | 2.22647 | -2.40135 | 0.11230 |
| C | 0.69264 | -2.49950 | 0.35032 |
| C | 2.68289 | -1.35242 | -0.94318 |
| H | 2.03302 | -1.42279 | -1.82184 |
| C | 4.13165 | -1.63050 | -1.37014 |
| C | -0.20275 | -2.76851 | -0.85904 |
| C | -1.72464 | -2.67653 | -0.61389 |
| H | 0.03943 | -3.78402 | -1.21070 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 0.08869 | -2.11185 | -1.68687 | H | 2.59103 | 2.11978 | -3.12008 |
| H | -1.96906 | -3.39967 | 0.17449 | H | 1.29231 | 1.02324 | -2.65122 |
| C | -2.48961 | -3.11402 | -1.87443 | H | 2.87928 | 0.38295 | -3.11641 |
| C | -2.14969 | -1.29817 | -0.03756 | H | 4.79659 | -1.61102 | -0.50384 |
| O | -3.57479 | -1.18227 | -0.15962 | H | 4.48896 | -0.88756 | -2.09063 |
| C | -1.49983 | -0.01416 | -0.59835 | H | 4.21183 | -2.61627 | -1.84299 |
| H | -1.88004 | -1.33500 | 1.02428 | H | 2.53006 | -3.39889 | -0.23810 |
| H | -2.23986 | -2.50649 | -2.75018 | O | 2.93137 | -2.20574 | 1.32784 |
| H | -3.56673 | -3.03976 | -1.71178 | C | 2.84606 | -0.88147 | 1.85120 |
| H | -2.24838 | -4.15663 | -2.11496 | H | 1.80179 | -0.66402 | 2.11034 |
| C | -1.75033 | 0.23777 | -2.09167 | O | 0.24064 | -2.43322 | 1.47753 |
| H | -0.42209 | -0.08057 | -0.42010 | C | 3.74954 | -0.81021 | 3.06092 |
| C | -2.05138 | 1.11045 | 0.30641 | H | 3.70601 | 0.19164 | 3.49699 |
| O | -3.47056 | 1.16223 | 0.14836 | H | 3.42698 | -1.54125 | 3.80709 |
| C | -1.47300 | 2.52396 | 0.06470 | H | 4.78030 | -1.03015 | 2.76736 |
| H | -1.80300 | 0.86010 | 1.34832 | ---------- | | | |
| H | -1.33370 | 1.19970 | -2.40688 | | | | |
| H | -2.82039 | 0.24042 | -2.31209 | Compound **5.29** | | | |
| H | -1.28038 | -0.53222 | -2.71111 | This structure was assigned as incorrect. | | | |
| H | -1.55557 | 2.78579 | -0.99313 | B3LYP/6-31g(d) | | | |
| C | 0.00401 | 2.47982 | 0.45455 | Gas phase. | | | |
| C | -2.19804 | 3.58042 | 0.91496 | | | | |
| C | -4.15556 | -0.05024 | 0.49036 | Electronic Energy: -1465.22292043 hartree. | | | |
| C | -5.55338 | 0.09245 | -0.09888 | | | | |
| C | -4.20562 | -0.24852 | 2.01348 | Free Energy: -1464.656498 hartree. | | | |
| H | -3.21540 | -0.36952 | 2.45964 | | | | |
| H | -4.78886 | -1.14466 | 2.24564 | C | 2.16126 | -2.47196 | 0.09159 |
| H | -4.68419 | 0.61657 | 2.48230 | C | 0.73914 | -2.61393 | -0.53077 |
| H | -6.13952 | -0.80889 | 0.10154 | C | 3.02749 | -1.43322 | -0.66829 |
| H | -5.48073 | 0.23592 | -1.18009 | H | 2.77313 | -1.53719 | -1.72667 |
| H | -6.06186 | 0.95526 | 0.34075 | C | 4.52449 | -1.69010 | -0.45958 |
| H | -2.06885 | 3.36710 | 1.98041 | C | -0.41708 | -3.03930 | 0.36857 |
| H | -3.26435 | 3.57716 | 0.68047 | C | -1.87244 | -2.69899 | -0.04989 |
| H | -1.79660 | 4.58022 | 0.71659 | H | -0.22208 | -2.69466 | 1.38883 |
| O | 0.38906 | 2.34823 | 1.59835 | H | -0.33010 | -4.13677 | 0.42511 |
| O | 0.82293 | 2.57305 | -0.61962 | H | -2.49191 | -3.21406 | 0.69882 |
| C | 2.27257 | 2.53030 | -0.39971 | C | -2.30729 | -3.27920 | -1.40609 |
| C | 2.84096 | 3.86027 | -0.87940 | C | -2.21429 | -1.20806 | 0.20000 |
| C | 2.83737 | 1.28367 | -1.12152 | O | -3.60750 | -1.03885 | -0.08644 |
| H | 2.43789 | 2.41773 | 0.67257 | C | -1.42422 | -0.07983 | -0.49656 |
| C | 2.49547 | 0.03212 | -0.28970 | H | -2.05145 | -1.06347 | 1.28255 |
| H | 3.93060 | 1.38743 | -1.10325 | H | -1.69872 | -2.92674 | -2.23676 |
| C | 2.37138 | 1.19181 | -2.58303 | H | -3.35325 | -3.02299 | -1.59498 |
| H | 2.41450 | 4.68434 | -0.29866 | H | -2.22632 | -4.37309 | -1.37817 |
| H | 2.62126 | 4.04148 | -1.93627 | C | -1.51012 | -0.07537 | -2.02898 |
| H | 3.92794 | 3.87519 | -0.74287 | H | -0.37763 | -0.17345 | -0.18924 |
| O | 3.28632 | 0.07777 | 0.90187 | C | -1.97924 | 1.21319 | 0.14205 |
| H | 1.43818 | 0.11433 | 0.00535 | O | -3.36488 | 1.31944 | -0.19173 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.26155 | 2.52115 | -0.25932 | H | 3.25856 | -1.08237 | 3.59741 |
| H | -1.86789 | 1.13687 | 1.23384 | | | | |
| H | -1.04779 | 0.82543 | -2.44555 | | | | |
| H | -2.55079 | -0.10375 | -2.35985 | | | | |
| H | -0.98256 | -0.93200 | -2.44952 | | | | |
| H | -1.18947 | 2.59573 | -1.34678 | | | | |
| C | 0.14640 | 2.46710 | 0.33326 | | | | |
| C | -1.99440 | 3.75859 | 0.28911 | | | | |
| C | -4.17303 | 0.22844 | 0.26357 | | | | |
| C | -5.47518 | 0.32749 | -0.52090 | | | | |
| C | -4.41900 | 0.31781 | 1.77811 | | | | |
| H | -3.49789 | 0.23358 | 2.36066 | | | | |
| H | -5.08939 | -0.48919 | 2.08874 | | | | |
| H | -4.88439 | 1.27786 | 2.02090 | C | 2.06901 | -2.48972 | 0.09714 |
| H | -6.14243 | -0.49476 | -0.24742 | C | 0.65369 | -2.57393 | -0.52098 |
| H | -5.26023 | 0.26983 | -1.59098 | C | 2.96363 | -1.47335 | -0.63825 |
| H | -5.97280 | 1.27827 | -0.30907 | H | 2.74880 | -1.57228 | -1.70553 |
| H | -2.02413 | 3.73254 | 1.38291 | C | 4.44010 | -1.74185 | -0.36825 |
| H | -3.01773 | 3.78127 | -0.09105 | C | -0.50287 | -2.98344 | 0.36982 |
| H | -1.48473 | 4.67861 | -0.01747 | C | -1.93829 | -2.64132 | -0.07552 |
| O | 0.35895 | 2.40423 | 1.52800 | H | -0.32807 | -2.61073 | 1.38447 |
| O | 1.11259 | 2.48714 | -0.61411 | H | -0.40824 | -4.07803 | 0.44658 |
| C | 2.51301 | 2.45884 | -0.17383 | H | -2.57857 | -3.17169 | 0.64298 |
| C | 3.13796 | 3.79143 | -0.56854 | C | -2.34111 | -3.17193 | -1.45305 |
| C | 3.20049 | 1.21078 | -0.77820 | C | -2.25639 | -1.16099 | 0.18811 |
| H | 2.50645 | 2.35493 | 0.91092 | O | -3.62263 | -0.93552 | -0.15177 |
| C | 2.56885 | -0.05092 | -0.16970 | C | -1.40856 | -0.06786 | -0.47480 |
| H | 4.24660 | 1.26061 | -0.44565 | H | -2.12633 | -1.03025 | 1.27550 |
| C | 3.16142 | 1.18058 | -2.31353 | H | -1.77104 | -2.73042 | -2.26769 |
| H | 2.64917 | 4.60981 | -0.03018 | H | -3.40429 | -2.97953 | -1.62303 |
| H | 3.04145 | 3.98556 | -1.64105 | H | -2.18455 | -4.25633 | -1.48734 |
| H | 4.20230 | 3.80187 | -0.30750 | C | -1.48221 | -0.03817 | -2.00006 |
| O | 2.77167 | -0.00609 | 1.25103 | H | -0.37466 | -0.20764 | -0.14903 |
| H | 1.49040 | 0.02048 | -0.36774 | C | -1.92776 | 1.23170 | 0.15514 |
| H | 3.59603 | 2.09092 | -2.73742 | O | -3.28777 | 1.39611 | -0.22127 |
| H | 2.13343 | 1.09682 | -2.68124 | C | -1.14812 | 2.49690 | -0.21623 |
| H | 3.73200 | 0.33485 | -2.70902 | H | -1.85054 | 1.14181 | 1.24912 |
| H | 4.79092 | -1.61508 | 0.59832 | H | -1.04864 | 0.88434 | -2.39968 |
| H | 5.13308 | -0.96784 | -1.01511 | H | -2.52207 | -0.09317 | -2.33474 |
| H | 4.79828 | -2.69106 | -0.81265 | H | -0.92669 | -0.86966 | -2.43446 |
| H | 2.61007 | -3.46756 | -0.03775 | H | -1.09863 | 2.62218 | -1.30008 |
| O | 2.17767 | -2.26391 | 1.50400 | C | 0.25915 | 2.33144 | 0.33700 |
| C | 1.93658 | -0.91967 | 1.91830 | C | -1.78234 | 3.73933 | 0.41645 |
| H | 0.88778 | -0.65827 | 1.69404 | C | -4.13897 | 0.33899 | 0.21147 |
| O | 0.63353 | -2.50496 | -1.74054 | C | -5.42689 | 0.50192 | -0.57096 |
| C | 2.21050 | -0.83675 | 3.40346 | C | -4.39098 | 0.42023 | 1.71659 |
| H | 2.00478 | 0.17722 | 3.75656 | H | -3.48307 | 0.28518 | 2.30893 |
| H | 1.57444 | -1.54326 | 3.94430 | H | -5.10419 | -0.35667 | 2.00584 |

---

Compound **5.29**

This structure was assigned as incorrect.

M06-2X/6-31g(d)

SMD implicit solvation in dimethylsulfoxide was used.

Electronic Energy: -1464.64493902 hartree.

Free Energy: -1464.070959 hartree.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -4.81693 | 1.39754 | 1.96133 | C | 2.24507 | -2.44756 | 0.06741 |
| H | -6.13193 | -0.28866 | -0.30173 | C | 0.82605 | -2.63062 | -0.54472 |
| H | -5.21228 | 0.44104 | -1.64133 | C | 3.07532 | -1.36531 | -0.67195 |
| H | -5.88018 | 1.47240 | -0.35253 | H | 2.82690 | -1.45312 | -1.73297 |
| H | -1.83582 | 3.62672 | 1.50407 | C | 4.57930 | -1.58247 | -0.47681 |
| H | -2.79405 | 3.87674 | 0.02933 | C | -0.32231 | -3.03869 | 0.36698 |
| H | -1.19641 | 4.63514 | 0.18879 | C | -1.78564 | -2.73149 | -0.04684 |
| O | 0.47862 | 2.10954 | 1.50780 | H | -0.13682 | -2.66280 | 1.37684 |
| O | 1.20996 | 2.47582 | -0.59697 | H | -0.21812 | -4.13292 | 0.45028 |
| C | 2.60214 | 2.40875 | -0.17748 | H | -2.38445 | -3.26578 | 0.70453 |
| C | 3.26069 | 3.69489 | -0.64051 | C | -2.21352 | -3.32553 | -1.39834 |
| C | 3.24214 | 1.12874 | -0.74203 | C | -2.16910 | -1.25045 | 0.20794 |
| H | 2.61290 | 2.34570 | 0.91103 | O | -3.57079 | -1.12355 | -0.08595 |
| C | 2.52700 | -0.08524 | -0.15725 | C | -1.40893 | -0.09808 | -0.48350 |
| H | 4.27868 | 1.12794 | -0.37830 | H | -2.01729 | -1.10498 | 1.28915 |
| C | 3.23941 | 1.08088 | -2.26841 | H | -1.65214 | -2.92848 | -2.24282 |
| H | 2.83683 | 4.54899 | -0.10413 | H | -3.27888 | -3.13938 | -1.56570 |
| H | 3.11266 | 3.85729 | -1.71160 | H | -2.06190 | -4.41259 | -1.38408 |
| H | 4.33578 | 3.65964 | -0.43769 | C | -1.46718 | -0.11105 | -2.01623 |
| O | 2.67029 | -0.04373 | 1.26066 | H | -0.36726 | -0.15622 | -0.15553 |
| H | 1.46091 | 0.02798 | -0.41034 | C | -2.01276 | 1.18518 | 0.13146 |
| H | 3.71522 | 1.96903 | -2.69319 | O | -3.40486 | 1.23617 | -0.20326 |
| H | 2.21594 | 1.02272 | -2.65712 | C | -1.35339 | 2.51817 | -0.30000 |
| H | 3.79089 | 0.20969 | -2.63432 | H | -1.90383 | 1.12901 | 1.22400 |
| H | 4.66119 | -1.63923 | 0.69844 | H | -1.02097 | 0.79524 | -2.43940 |
| H | 5.07579 | -1.04051 | -0.91931 | H | -2.49940 | -0.17164 | -2.37171 |
| H | 4.71254 | -2.75567 | -0.67959 | H | -0.90945 | -0.95868 | -2.41742 |
| H | 2.48403 | -3.49823 | -0.03988 | H | -1.26379 | 2.55613 | -1.38800 |
| O | 2.07340 | -2.28032 | 1.50097 | C | 0.04595 | 2.57744 | 0.31348 |
| C | 1.79569 | -0.94346 | 1.88133 | C | -2.16054 | 3.73496 | 0.18124 |
| H | 0.76308 | -0.68901 | 1.58319 | C | -4.17268 | 0.12320 | 0.27439 |
| O | 0.54816 | -2.44259 | -1.72502 | C | -5.49236 | 0.17968 | -0.48355 |
| C | 1.97012 | -0.84535 | 3.37378 | C | -4.39503 | 0.21104 | 1.79099 |
| H | 1.74789 | 0.17222 | 3.70302 | H | -3.46367 | 0.15580 | 2.36083 |
| H | 1.29266 | -1.53970 | 3.87711 | H | -5.03754 | -0.61366 | 2.11618 |
| H | 3.00140 | -1.09442 | 3.63947 | H | -4.88906 | 1.15557 | 2.04088 |
| ---------- | | | | H | -6.12887 | -0.66383 | -0.19938 |
| | | | | H | -5.30420 | 0.13295 | -1.56038 |
| Compound **5.29** | | | | H | -6.02297 | 1.10987 | -0.25796 |
| This structure was assigned as incorrect. | | | | H | -2.26531 | 3.72959 | 1.27102 |
| B3LYP/6-31g(d) | | | | H | -3.15835 | 3.72362 | -0.26300 |
| SMD implicit solvation in dimethylsulfoxide was used. | | | | H | -1.66217 | 4.66683 | -0.10934 |
| | | | | O | 0.24182 | 2.72198 | 1.50630 |
| | | | | O | 1.02451 | 2.45665 | -0.60732 |
| Electronic Energy: -1465.24347050 hartree. | | | | C | 2.42228 | 2.49855 | -0.14731 |
| | | | | C | 2.99431 | 3.85728 | -0.52531 |
| Free Energy: -1464.676517 hartree. | | | | C | 3.17006 | 1.28260 | -0.74124 |
| | | | | H | 2.40300 | 2.39460 | 0.93683 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.57668 | -0.00608 | -0.15055 | C | -1.45297 | 0.00766 | -0.55203 |
| H | 4.20637 | 1.37746 | -0.39030 | H | -1.92762 | -1.34857 | 1.01105 |
| C | 3.17016 | 1.25660 | -2.27599 | H | -2.18610 | -2.28713 | -2.81301 |
| H | 2.45489 | 4.65333 | -0.00013 | H | -3.54117 | -2.89891 | -1.85350 |
| H | 2.92282 | 4.04951 | -1.60047 | H | -2.20434 | -3.97552 | -2.29501 |
| H | 4.04935 | 3.91395 | -0.23386 | C | -1.65797 | 0.30471 | -2.03546 |
| O | 2.77493 | 0.02208 | 1.27650 | H | -0.38451 | -0.09555 | -0.34316 |
| H | 1.49759 | 0.03537 | -0.34558 | C | -1.99982 | 1.11532 | 0.35534 |
| H | 3.57115 | 2.18910 | -2.68574 | O | -3.40259 | 1.21555 | 0.15649 |
| H | 2.15914 | 1.12172 | -2.67656 | C | -1.37616 | 2.50100 | 0.15048 |
| H | 3.79452 | 0.44200 | -2.65591 | H | -1.78698 | 0.83805 | 1.39957 |
| H | 4.85287 | -1.53489 | 0.58178 | H | -1.25764 | 1.28773 | -2.30246 |
| H | 5.16298 | -0.82433 | -1.01129 | H | -2.72210 | 0.28731 | -2.28874 |
| H | 4.88047 | -2.56400 | -0.86198 | H | -1.14488 | -0.42911 | -2.66306 |
| H | 2.72391 | -3.42480 | -0.08566 | H | -1.50511 | 2.82700 | -0.88424 |
| O | 2.26831 | -2.26245 | 1.48568 | C | 0.10789 | 2.36006 | 0.45070 |
| C | 1.96425 | -0.93675 | 1.91780 | C | -1.99620 | 3.52558 | 1.10132 |
| H | 0.91128 | -0.71497 | 1.67957 | C | -4.11826 | 0.01744 | 0.44649 |
| O | 0.72469 | -2.57891 | -1.76161 | C | -5.50072 | 0.21003 | -0.14435 |
| C | 2.20950 | -0.87073 | 3.40822 | C | -4.19138 | -0.22636 | 1.95371 |
| H | 1.96695 | 0.12892 | 3.78121 | H | -3.21042 | -0.36661 | 2.41321 |
| H | 1.58054 | -1.60053 | 3.92703 | H | -4.78817 | -1.12232 | 2.14612 |
| H | 3.26000 | -1.08811 | 3.62704 | H | -4.67398 | 0.62771 | 2.43722 |
| ---------- | | | | H | -6.10719 | -0.68275 | 0.02870 |
| | | | | H | -5.41642 | 0.38269 | -1.22061 |
| Compound **5.29** | | | | H | -5.99296 | 1.06873 | 0.31950 |
| This structure was assigned as correct. | | | | H | -1.86726 | 3.20692 | 2.14040 |
| M06-2X/6-31g(d) | | | | H | -3.06447 | 3.62260 | 0.89668 |
| SMD implicit solvation in dimethylsulfoxide was used. | | | | H | -1.52727 | 4.50664 | 0.97910 |
| | | | | O | 0.53524 | 2.08480 | 1.55061 |
| | | | | O | 0.87443 | 2.55287 | -0.63094 |
| Electronic Energy: -1464.64709580 hartree. | | | | C | 2.32085 | 2.48408 | -0.48624 |
| | | | | C | 2.88197 | 3.76046 | -1.08325 |
| Free Energy: -1464.074465 hartree. | | | | C | 2.82542 | 1.19715 | -1.15850 |
| | | | | H | 2.54902 | 2.43353 | 0.58012 |
| C | 2.16481 | -2.40547 | 0.16707 | C | 2.45095 | 0.00079 | -0.28556 |
| C | 0.63148 | -2.48566 | 0.33879 | H | 3.92112 | 1.26799 | -1.18436 |
| C | 2.66315 | -1.39398 | -0.88621 | C | 2.28734 | 1.03619 | -2.58007 |
| H | 2.06137 | -1.49472 | -1.79356 | H | 2.51368 | 4.62978 | -0.53073 |
| C | 4.12929 | -1.65681 | -1.22181 | H | 2.59656 | 3.87726 | -2.13253 |
| C | -0.21212 | -2.66922 | -0.90956 | H | 3.97422 | 3.75024 | -1.01877 |
| C | -1.72977 | -2.60858 | -0.69076 | O | 3.18120 | 0.08096 | 0.93404 |
| H | 0.06384 | -3.64615 | -1.33381 | H | 1.38375 | 0.10276 | -0.03746 |
| H | 0.08796 | -1.93413 | -1.66485 | H | 2.43726 | 1.94740 | -3.16619 |
| H | -1.99220 | -3.37994 | 0.04453 | H | 1.21334 | 0.81752 | -2.56767 |
| C | -2.45903 | -2.95448 | -1.99053 | H | 2.79391 | 0.22145 | -3.10544 |
| C | -2.15364 | -1.26559 | -0.05943 | H | 4.74566 | -1.57963 | -0.32207 |
| O | -3.56061 | -1.09907 | -0.23094 | H | 4.50488 | -0.93751 | -1.95711 |

| | | | |
|---|---|---|---|
| H | 4.25425 | -2.66026 | -1.64148 |
| H | 2.46998 | -3.41539 | -0.14167 |
| O | 2.80534 | -2.17065 | 1.40760 |
| C | 2.67325 | -0.83849 | 1.87081 |
| H | 1.60806 | -0.61484 | 2.03185 |
| O | 0.14155 | -2.48405 | 1.44935 |
| C | 3.46740 | -0.71788 | 3.14437 |
| H | 3.38148 | 0.29639 | 3.54179 |
| H | 3.08965 | -1.42448 | 3.88714 |
| H | 4.51978 | -0.93711 | 2.94280 |

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Compound **5.29**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in dimethylsulfoxide was used.

Electronic Energy: -1465.24587141 hartree.
Free Energy: -1464.679536 hartree.

| | | | |
|---|---|---|---|
| C | 2.31104 | -2.37968 | 0.09821 |
| C | 0.78237 | -2.55501 | 0.31674 |
| C | 2.75122 | -1.30397 | -0.93166 |
| H | 2.12707 | -1.39159 | -1.82501 |
| C | 4.21629 | -1.52524 | -1.33164 |
| C | -0.09948 | -2.73473 | -0.91186 |
| C | -1.62211 | -2.68575 | -0.66948 |
| H | 0.16436 | -3.71904 | -1.32988 |
| H | 0.18528 | -2.01607 | -1.68629 |
| H | -1.85435 | -3.42778 | 0.10517 |
| C | -2.36884 | -3.12309 | -1.93992 |
| C | -2.07692 | -1.32766 | -0.07050 |
| O | -3.51383 | -1.27422 | -0.13246 |
| C | -1.50231 | -0.01426 | -0.64514 |
| H | -1.76881 | -1.35738 | 0.98154 |
| H | -2.10773 | -2.51709 | -2.81343 |
| H | -3.45061 | -3.05985 | -1.79514 |
| H | -2.11882 | -4.16482 | -2.17616 |
| C | -1.79570 | 0.21972 | -2.13271 |
| H | -0.41924 | -0.03361 | -0.49708 |
| C | -2.07579 | 1.08685 | 0.27380 |
| O | -3.50385 | 1.07333 | 0.16695 |
| C | -1.57144 | 2.52807 | 0.00930 |
| H | -1.78832 | 0.85046 | 1.30875 |
| H | -1.45393 | 1.20793 | -2.45787 |
| H | -2.86681 | 0.15057 | -2.34281 |
| H | -1.27894 | -0.51578 | -2.75617 |
| H | -1.63713 | 2.75534 | -1.05750 |
| C | -0.10323 | 2.59086 | 0.43266 |
| C | -2.37717 | 3.56887 | 0.80033 |
| C | -4.11722 | -0.16849 | 0.54257 |
| C | -5.54602 | -0.09000 | 0.02075 |
| C | -4.09265 | -0.36595 | 2.06555 |
| H | -3.08110 | -0.46497 | 2.46812 |
| H | -4.64524 | -1.27472 | 2.32564 |
| H | -4.57208 | 0.48555 | 2.55924 |
| H | -6.08295 | -1.01716 | 0.24315 |
| H | -5.53895 | 0.06334 | -1.06260 |
| H | -6.07693 | 0.74311 | 0.49163 |
| H | -2.33893 | 3.36174 | 1.87458 |
| H | -3.42185 | 3.55746 | 0.48171 |
| H | -1.97537 | 4.57475 | 0.63364 |
| O | 0.25754 | 2.66415 | 1.59276 |
| O | 0.73590 | 2.54023 | -0.62141 |
| C | 2.18547 | 2.55637 | -0.37467 |
| C | 2.71851 | 3.90718 | -0.83025 |
| C | 2.80544 | 1.33492 | -1.09099 |
| H | 2.33247 | 2.44615 | 0.69993 |
| C | 2.49292 | 0.06565 | -0.27538 |
| H | 3.89276 | 1.48375 | -1.05683 |
| C | 2.37104 | 1.23229 | -2.56065 |
| H | 2.24542 | 4.71401 | -0.25972 |
| H | 2.53097 | 4.08589 | -1.89406 |
| H | 3.79932 | 3.95770 | -0.65631 |
| O | 3.25095 | 0.13316 | 0.94604 |
| H | 1.42660 | 0.10253 | -0.00625 |
| H | 2.54980 | 2.17765 | -3.08376 |
| H | 1.30524 | 1.00036 | -2.65389 |
| H | 2.93443 | 0.45908 | -3.09103 |
| H | 4.87105 | -1.50173 | -0.45616 |
| H | 4.56225 | -0.75928 | -2.03373 |
| H | 4.33554 | -2.49990 | -1.81969 |
| H | 2.65442 | -3.36102 | -0.25837 |
| O | 2.98985 | -2.17178 | 1.33579 |
| C | 2.82812 | -0.85954 | 1.86603 |
| H | 1.76521 | -0.69373 | 2.09266 |
| O | 0.33418 | -2.64121 | 1.44820 |
| C | 3.67577 | -0.75696 | 3.11298 |
| H | 3.56898 | 0.23725 | 3.55786 |
| H | 3.35556 | -1.50450 | 3.84511 |
| H | 4.72977 | -0.92662 | 2.86951 |

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Compound **5.30**

This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -169.950623 kJ.

| | | | |
|---|---|---|---|
| C | 2.08140 | -4.26250 | 1.39770 |
| C | 0.87640 | -5.17480 | 1.65900 |
| O | 0.23150 | -4.99620 | 2.69260 |
| C | 0.51280 | -6.22290 | 0.67080 |
| C | 0.81960 | -6.07640 | -0.63870 |
| C | -0.19920 | -7.43430 | 1.25530 |
| H | 1.32350 | -5.18460 | -0.97840 |
| C | 0.53250 | -7.06770 | -1.75590 |
| H | -0.32860 | -7.68290 | -1.49610 |
| C | 1.74340 | -7.97130 | -2.04780 |
| H | 0.23840 | -6.51760 | -2.65040 |
| H | 2.02550 | -8.45120 | -1.11210 |
| C | 2.95270 | -7.24430 | -2.69460 |
| H | 1.43180 | -8.79840 | -2.68730 |
| C | 2.83910 | -7.31810 | -4.22870 |
| C | 4.30820 | -7.78110 | -2.15670 |
| H | 2.91200 | -6.18730 | -2.43020 |
| H | 1.85630 | -6.98740 | -4.56570 |
| H | 2.98720 | -8.33680 | -4.58900 |
| H | 3.57190 | -6.67830 | -4.72010 |
| O | 4.42870 | -7.34550 | -0.80650 |
| C | 5.54330 | -7.23390 | -2.88930 |
| H | 4.31960 | -8.86950 | -2.23460 |
| H | 5.55080 | -6.14380 | -2.89780 |
| H | 5.58530 | -7.58320 | -3.92060 |
| H | 6.45920 | -7.56970 | -2.40220 |
| C | 4.38480 | -8.22020 | 0.22220 |
| O | 4.47340 | -9.44060 | 0.10200 |
| C | 4.12770 | -7.56080 | 1.50940 |
| C | 4.26160 | -6.23330 | 1.70200 |
| H | 3.75070 | -8.18790 | 2.30350 |
| C | 3.80900 | -5.50390 | 2.95610 |
| O | 2.89210 | -6.35620 | 3.64240 |
| C | 3.08910 | -4.18250 | 2.56710 |
| C | 5.04570 | -5.19070 | 3.81850 |
| Si | 2.34380 | -6.36670 | 5.25390 |
| C | 1.93720 | -4.62040 | 5.86990 |
| C | 0.75990 | -7.41120 | 5.30390 |
| C | 3.70360 | -7.11540 | 6.35200 |
| H | 0.33690 | -7.41660 | 6.30750 |
| H | 0.01590 | -6.92900 | 4.66880 |
| H | 3.29360 | -7.36880 | 7.32930 |
| H | 4.46740 | -6.36120 | 6.53670 |
| H | 1.15370 | -4.19090 | 5.24420 |
| H | 2.80340 | -3.96860 | 5.77210 |
| H | 4.79040 | -4.63610 | 4.72010 |
| H | 5.76620 | -4.58580 | 3.26700 |
| H | 5.56240 | -6.10060 | 4.12150 |
| H | 3.84420 | -3.45250 | 2.27410 |
| H | 2.60020 | -3.73980 | 3.43150 |
| H | 1.69370 | -3.26600 | 1.18880 |
| H | 2.61250 | -4.57700 | 0.50300 |
| H | -1.24820 | -7.20160 | 1.43880 |
| H | 0.25340 | -7.71440 | 2.20670 |
| H | -0.14180 | -8.30800 | 0.60890 |
| H | 4.63670 | -5.60620 | 0.90570 |
| C | 4.37070 | -8.35440 | 5.73460 |
| H | 3.68540 | -9.19690 | 5.67310 |
| H | 5.22290 | -8.67490 | 6.33390 |
| H | 4.73120 | -8.15540 | 4.72560 |
| C | 0.96400 | -8.85320 | 4.82280 |
| H | 0.00550 | -9.34330 | 4.65200 |
| H | 1.49980 | -9.44410 | 5.56390 |
| H | 1.52680 | -8.88520 | 3.88880 |
| C | 1.47210 | -4.62260 | 7.33190 |
| H | 0.57220 | -5.22530 | 7.45930 |
| H | 1.24150 | -3.61170 | 7.66840 |
| H | 2.24100 | -5.02510 | 7.99220 |

---

Compound **5.30**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -169.635208 kJ.

| | | | |
|---|---|---|---|
| C | 1.04730 | -4.85520 | 2.45690 |
| C | 0.90860 | -4.83550 | 0.93000 |
| O | 1.08150 | -3.75150 | 0.37110 |
| C | 0.59130 | -6.07750 | 0.17380 |
| C | 0.69810 | -6.04690 | -1.17360 |
| C | 0.19560 | -7.31230 | 0.97500 |
| H | 1.01580 | -5.13100 | -1.65450 |
| C | 0.48580 | -7.20280 | -2.13700 |
| H | -0.36230 | -7.80570 | -1.81330 |
| C | 1.74180 | -8.08250 | -2.26010 |
| H | 0.20660 | -6.79840 | -3.11050 |
| H | 1.94680 | -8.49710 | -1.27450 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.98800 | -7.34680 | -2.82210 | C | 0.14170 | -7.79210 | 5.31020 |
| H | 1.51730 | -8.95480 | -2.87530 | H | 0.25490 | -7.70990 | 4.22870 |
| C | 3.06860 | -7.55090 | -4.34590 | H | -0.55390 | -8.60740 | 5.50970 |
| C | 4.28520 | -7.76630 | -2.08280 | H | -0.31400 | -6.86940 | 5.67070 |
| H | 2.87750 | -6.27480 | -2.65810 | C | 1.76470 | -5.12550 | 7.85980 |
| H | 2.12230 | -7.29680 | -4.82440 | H | 1.02160 | -5.89470 | 8.07310 |
| H | 3.30000 | -8.58670 | -4.59650 | H | 1.38480 | -4.18240 | 8.25320 |
| H | 3.83060 | -6.91720 | -4.79930 | H | 2.67150 | -5.37380 | 8.41250 |
| O | 4.18600 | -7.31100 | -0.73490 | | | | |
| C | 5.56580 | -7.13730 | -2.65410 | --- | | | |
| H | 4.38450 | -8.85150 | -2.13750 | | | | |
| H | 5.49380 | -6.04990 | -2.68620 | Compound **5.30** | | | |
| H | 5.77380 | -7.49480 | -3.66200 | This structure was assigned as correct. | | | |
| H | 6.42870 | -7.39600 | -2.04000 | M06-2X/6-31g(d) | | | |
| C | 4.19380 | -8.18000 | 0.29990 | SMD implicit solvation in methanol was used. | | | |
| O | 4.37430 | -9.39110 | 0.18690 | | | | |
| C | 3.92350 | -7.54210 | 1.59710 | | | | |
| C | 3.80550 | -6.21100 | 1.77810 | Electronic Energy: -1490.44011321 hartree. | | | |
| H | 3.80650 | -8.20850 | 2.43820 | | | | |
| C | 3.47460 | -5.56470 | 3.11410 | Free Energy: -1489.900606 hartree. | | | |
| O | 2.89290 | -6.55890 | 3.95790 | | | | |
| C | 2.44660 | -4.42010 | 2.94730 | C | 0.51194 | 2.26494 | -0.21561 |
| C | 4.78050 | -5.00830 | 3.70900 | C | -0.91358 | 2.33765 | -0.74651 |
| Si | 2.71920 | -6.64280 | 5.64670 | O | -1.10218 | 2.62716 | -1.92302 |
| C | 2.04060 | -5.02070 | 6.35430 | C | -2.10572 | 2.15245 | 0.13545 |
| C | 1.49550 | -8.04630 | 5.98520 | C | -2.00992 | 1.49765 | 1.30562 |
| C | 4.39030 | -7.07130 | 6.42830 | C | -3.39042 | 2.65846 | -0.46532 |
| H | 1.90710 | -8.98680 | 5.61990 | H | -1.03666 | 1.12056 | 1.61606 |
| H | 1.35590 | -8.17210 | 7.05840 | C | -3.12358 | 1.12882 | 2.24204 |
| H | 4.26520 | -7.24690 | 7.49640 | H | -2.78683 | 1.31400 | 3.26876 |
| H | 5.07400 | -6.22810 | 6.34190 | C | -3.47682 | -0.36255 | 2.09090 |
| H | 1.12090 | -4.74810 | 5.83720 | H | -4.01639 | 1.74022 | 2.07711 |
| H | 2.74580 | -4.20950 | 6.17850 | H | -2.54641 | -0.94225 | 2.11451 |
| H | 4.61800 | -4.49140 | 4.65390 | C | -4.26285 | -0.65284 | 0.79719 |
| H | 5.24460 | -4.29090 | 3.03110 | H | -4.07054 | -0.68545 | 2.95514 |
| H | 5.50590 | -5.80380 | 3.88230 | C | -5.76783 | -0.58283 | 1.05175 |
| H | 2.31930 | -3.90420 | 3.89600 | C | -3.85859 | -2.00472 | 0.20080 |
| H | 2.85730 | -3.65690 | 2.28350 | H | -4.00859 | 0.10814 | 0.04874 |
| H | 0.31220 | -4.14460 | 2.83320 | H | -6.01817 | 0.34870 | 1.57198 |
| H | 0.77560 | -5.81500 | 2.88830 | H | -6.09621 | -1.41643 | 1.68501 |
| H | -0.04940 | -8.16260 | 0.34220 | H | -6.34405 | -0.60900 | 0.12221 |
| H | -0.67760 | -7.10300 | 1.59340 | O | -2.42531 | -1.98126 | -0.05809 |
| H | 1.01300 | -7.62590 | 1.62480 | C | -4.66632 | -2.45971 | -1.00595 |
| H | 3.92330 | -5.53400 | 0.94310 | H | -3.93120 | -2.77203 | 0.97992 |
| C | 5.01800 | -8.30960 | 5.77490 | H | -4.83434 | -1.65293 | -1.72196 |
| H | 4.38470 | -9.18820 | 5.90110 | H | -5.63669 | -2.83488 | -0.66759 |
| H | 5.98960 | -8.53520 | 6.21480 | H | -4.15019 | -3.28045 | -1.51364 |
| H | 5.16420 | -8.15890 | 4.70450 | C | -1.91720 | -1.15846 | -0.98173 |

| | | | |
|---|---|---|---|
| O | -2.57277 | -0.59912 | -1.84360 |
| C | -0.46485 | -0.96811 | -0.77993 |
| C | 0.23669 | -0.23593 | -1.64638 |
| H | -0.03215 | -1.35256 | 0.13780 |
| C | 1.63056 | 0.27302 | -1.40197 |
| O | 2.08838 | -0.27942 | -0.17802 |
| C | 1.52658 | 1.81246 | -1.26747 |
| C | 2.54316 | -0.08614 | -2.57561 |
| Si | 3.65157 | -0.47542 | 0.41912 |
| C | 4.52323 | -1.88412 | -0.47743 |
| C | 4.64577 | 1.12121 | 0.32671 |
| C | 3.35487 | -0.94258 | 2.21443 |
| H | 4.83766 | 1.38460 | -0.72182 |
| H | 4.04526 | 1.94065 | 0.74375 |
| H | 4.32041 | -1.17735 | 2.68292 |
| H | 2.77123 | -1.87227 | 2.24605 |
| H | 5.44090 | -2.12278 | 0.07827 |
| H | 4.85012 | -1.55455 | -1.47175 |
| H | 2.65790 | -1.17127 | -2.66015 |
| H | 2.11999 | 0.29044 | -3.51178 |
| H | 3.53117 | 0.36974 | -2.44573 |
| H | 1.26006 | 2.23862 | -2.23986 |
| H | 2.52349 | 2.18531 | -1.01180 |
| H | 0.58989 | 1.64528 | 0.68012 |
| H | 0.74335 | 3.29107 | 0.10234 |
| H | -3.64062 | 2.08160 | -1.36284 |
| H | -3.28729 | 3.70301 | -0.77822 |
| H | -4.22746 | 2.58682 | 0.23086 |
| H | -0.24776 | 0.12772 | -2.55199 |
| C | 2.63241 | 0.15062 | 3.00935 |
| H | 3.20653 | 1.08467 | 3.02039 |
| H | 2.46604 | -0.14416 | 4.05154 |
| H | 1.65252 | 0.37240 | 2.57049 |
| C | 5.97622 | 1.01549 | 1.08632 |
| H | 6.54905 | 1.94700 | 1.02238 |
| H | 6.60761 | 0.21526 | 0.68330 |
| H | 5.81330 | 0.80319 | 2.14916 |
| C | 3.64981 | -3.14001 | -0.59195 |
| H | 3.38018 | -3.52652 | 0.39760 |
| H | 4.16305 | -3.94509 | -1.12916 |
| H | 2.71352 | -2.93052 | -1.12217 |

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Compound **5.30**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1490.98831636 hartree.
Free Energy: -1490.457482 hartree.

| | | | |
|---|---|---|---|
| C | 0.25646 | 2.26127 | -0.07595 |
| C | -1.13026 | 2.65035 | -0.61068 |
| O | -1.20922 | 3.16643 | -1.72018 |
| C | -2.38271 | 2.48001 | 0.19261 |
| C | -2.45085 | 1.57332 | 1.18813 |
| C | -3.54430 | 3.30391 | -0.31139 |
| H | -1.54908 | 1.01666 | 1.43363 |
| C | -3.65201 | 1.13667 | 1.97957 |
| H | -3.42606 | 1.25792 | 3.04921 |
| C | -3.99719 | -0.35173 | 1.72700 |
| H | -4.52634 | 1.76225 | 1.77207 |
| H | -3.09896 | -0.95383 | 1.89988 |
| C | -4.58513 | -0.63474 | 0.31547 |
| H | -4.71821 | -0.67384 | 2.48942 |
| C | -6.11302 | -0.78873 | 0.38815 |
| C | -3.90170 | -1.84797 | -0.34727 |
| H | -4.35987 | 0.22273 | -0.33354 |
| H | -6.55325 | 0.05991 | 0.92460 |
| H | -6.39532 | -1.70081 | 0.92993 |
| H | -6.57643 | -0.82544 | -0.60280 |
| O | -2.51691 | -1.45894 | -0.57884 |
| C | -4.47291 | -2.25640 | -1.70082 |
| H | -3.89669 | -2.70347 | 0.33440 |
| H | -4.48953 | -1.40757 | -2.39427 |
| H | -5.49243 | -2.64002 | -1.59685 |
| H | -3.85763 | -3.04710 | -2.14133 |
| C | -1.53226 | -2.09348 | 0.10439 |
| O | -1.71558 | -3.03438 | 0.85506 |
| C | -0.20469 | -1.47433 | -0.10779 |
| C | 0.05955 | -0.52080 | -1.00901 |
| H | 0.56764 | -1.83350 | 0.56297 |
| C | 1.39460 | 0.17596 | -1.16659 |
| O | 2.20895 | -0.17770 | -0.05128 |
| C | 1.18373 | 1.71560 | -1.18169 |
| C | 2.02599 | -0.26606 | -2.50283 |
| Si | 3.85669 | -0.31992 | 0.25150 |
| C | 4.81846 | 1.21745 | -0.32422 |
| C | 3.94683 | -0.49406 | 2.13426 |
| C | 4.58969 | -1.86543 | -0.57492 |
| H | 3.38630 | -1.39500 | 2.41951 |
| H | 4.99146 | -0.69672 | 2.41274 |
| H | 5.63882 | -1.94181 | -0.25196 |
| H | 4.63190 | -1.70572 | -1.66134 |
| H | 4.33984 | 2.10989 | 0.10263 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 4.72151 | 1.32238 | -1.41400 | C | 4.40439 | 0.15357 | -0.39760 |
| H | 2.94785 | 0.29261 | -2.70098 | H | 4.12790 | 1.48325 | -2.06994 |
| H | 1.33903 | -0.07894 | -3.33482 | C | 5.86645 | 0.59900 | -0.40831 |
| H | 2.25572 | -1.33522 | -2.48196 | C | 4.25801 | -1.27385 | -0.93964 |
| H | 2.17732 | 2.16701 | -1.10314 | H | 4.05945 | 0.14328 | 0.64561 |
| H | 0.77514 | 2.02407 | -2.14963 | H | 5.94314 | 1.65304 | -0.11966 |
| H | 0.66822 | 3.20258 | 0.31499 | H | 6.29646 | 0.49720 | -1.41250 |
| H | 0.21676 | 1.57891 | 0.77488 | H | 6.47952 | 0.01859 | 0.28757 |
| H | -3.79235 | 3.02763 | -1.34160 | O | 2.85477 | -1.65108 | -0.85033 |
| H | -3.27694 | 4.36647 | -0.33822 | C | 5.19133 | -2.31315 | -0.33617 |
| H | -4.43614 | 3.18997 | 0.30762 | H | 4.41423 | -1.25188 | -2.02391 |
| H | -0.72613 | -0.18737 | -1.68402 | H | 5.27057 | -2.22127 | 0.74847 |
| C | 3.86257 | -3.18835 | -0.27190 | H | 6.18813 | -2.19716 | -0.77175 |
| H | 3.86179 | -3.41030 | 0.80165 | H | 4.83471 | -3.31851 | -0.58023 |
| H | 4.33886 | -4.03605 | -0.77945 | C | 2.27119 | -1.76074 | 0.34984 |
| H | 2.81617 | -3.15530 | -0.59582 | O | 2.87552 | -1.95324 | 1.39002 |
| C | 3.41790 | 0.71270 | 2.92915 | C | 0.81410 | -1.53326 | 0.25132 |
| H | 2.36977 | 0.91624 | 2.68399 | C | 0.06568 | -1.52629 | 1.35536 |
| H | 3.47900 | 0.54247 | 4.01102 | H | 0.42082 | -1.24630 | -0.71807 |
| H | 3.98940 | 1.62271 | 2.70948 | C | -1.35734 | -1.03994 | 1.42621 |
| C | 6.31342 | 1.21017 | 0.05281 | O | -1.70299 | -0.53337 | 0.14768 |
| H | 6.81894 | 2.11991 | -0.29301 | C | -1.41486 | 0.08827 | 2.48311 |
| H | 6.83937 | 0.35734 | -0.39222 | C | -2.27180 | -2.18610 | 1.86781 |
| H | 6.45590 | 1.15209 | 1.13838 | Si | -3.18047 | -0.44174 | -0.65681 |
| --- | | | | C | -4.42005 | 0.58559 | 0.31892 |
| | | | | C | -2.70865 | 0.37560 | -2.28331 |
| Compound **5.30** | | | | C | -3.89262 | -2.14566 | -1.03636 |
| This structure was assigned as incorrect. | | | | H | -2.14884 | -0.35985 | -2.87732 |
| M06-2X/6-31g(d) | | | | H | -3.62534 | 0.58028 | -2.85338 |
| SMD implicit solvation in methanol was used. | | | | H | -4.74352 | -1.99223 | -1.71585 |
| | | | | H | -4.31398 | -2.59501 | -0.12850 |
| | | | | H | -3.95556 | 1.54285 | 0.58735 |
| Electronic Energy: -1490.43579573 hartree. | | | | H | -4.64236 | 0.07826 | 1.26785 |
| Free Energy: -1489.898682 hartree. | | | | H | -2.28256 | -2.98418 | 1.12041 |
| | | | | H | -1.91843 | -2.60568 | 2.81438 |
| | | | | H | -3.29389 | -1.82090 | 2.02084 |
| C | -0.31593 | 1.14897 | 2.37252 | H | -1.33644 | -0.37600 | 3.47208 |
| C | -0.49660 | 2.12622 | 1.22683 | H | -2.40247 | 0.55906 | 2.42155 |
| O | -1.61727 | 2.57822 | 1.01484 | H | -0.35828 | 1.78173 | 3.26990 |
| C | 0.66135 | 2.62964 | 0.42967 | H | 0.67082 | 0.68580 | 2.38091 |
| C | 1.84209 | 1.98269 | 0.42765 | H | 1.23597 | 4.55301 | -0.37499 |
| C | 0.39320 | 3.85793 | -0.40834 | H | -0.49442 | 4.37964 | -0.04601 |
| H | 1.96842 | 1.09381 | 1.04437 | H | 0.21577 | 3.59974 | -1.45922 |
| C | 3.03173 | 2.34122 | -0.41409 | H | 0.51636 | -1.81245 | 2.30618 |
| H | 2.78469 | 3.15787 | -1.09692 | C | -2.88735 | -3.10046 | -1.69293 |
| C | 3.53655 | 1.12790 | -1.21656 | H | -2.57274 | -2.72913 | -2.67446 |
| H | 3.83887 | 2.70410 | 0.23990 | H | -3.31432 | -4.09822 | -1.84312 |
| H | 2.66752 | 0.60591 | -1.63395 | H | -1.98061 | -3.21690 | -1.08750 |

| | | | |
|---|---|---|---|
| C | -1.87350 | 1.65215 | -2.13883 |
| H | -1.60617 | 2.07242 | -3.11547 |
| H | -0.94185 | 1.44470 | -1.60015 |
| H | -2.41071 | 2.42796 | -1.58178 |
| C | -5.72288 | 0.83213 | -0.45352 |
| H | -6.22317 | -0.10775 | -0.71356 |
| H | -5.53691 | 1.37589 | -1.38679 |
| H | -6.43132 | 1.42673 | 0.13377 |

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Compound **5.30**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
SMD implicit solvation in methanol was used.

Electronic Energy: -1491.01203561 hartree.
Free Energy: -1490.481787 hartree.

| | | | |
|---|---|---|---|
| C | 0.56863 | 1.94594 | 0.35408 |
| C | -0.35864 | 3.14868 | 0.22119 |
| O | 0.13968 | 4.26882 | 0.06170 |
| C | -1.84329 | 3.00440 | 0.22904 |
| C | -2.40831 | 1.79402 | 0.43521 |
| C | -2.60898 | 4.28087 | -0.01833 |
| H | -1.74631 | 0.94975 | 0.59489 |
| C | -3.85485 | 1.39641 | 0.42433 |
| H | -4.03781 | 0.78984 | 1.32129 |
| C | -4.18268 | 0.55980 | -0.85576 |
| H | -4.52026 | 2.26103 | 0.49221 |
| H | -4.79455 | 1.17656 | -1.52497 |
| C | -4.92615 | -0.77793 | -0.64218 |
| H | -3.25822 | 0.35776 | -1.40486 |
| C | -6.32379 | -0.55500 | -0.04257 |
| C | -4.14652 | -1.81163 | 0.20221 |
| H | -5.05414 | -1.21342 | -1.64390 |
| H | -6.90466 | 0.12519 | -0.67656 |
| H | -6.26450 | -0.11166 | 0.95930 |
| H | -6.89041 | -1.48851 | 0.04231 |
| O | -2.73330 | -1.70764 | -0.17364 |
| C | -4.60800 | -3.24772 | -0.02073 |
| H | -4.20896 | -1.55703 | 1.26473 |
| H | -4.46395 | -3.53580 | -1.06865 |
| H | -5.66974 | -3.35710 | 0.22242 |
| H | -4.04423 | -3.93821 | 0.61321 |
| C | -1.80147 | -2.04389 | 0.73764 |
| O | -2.06111 | -2.60156 | 1.79909 |
| C | -0.43424 | -1.61346 | 0.38171 |
| C | -0.14979 | -0.87394 | -0.69867 |
| H | 0.31961 | -1.85505 | 1.12378 |
| C | 1.16470 | -0.20220 | -1.01943 |
| O | 2.11435 | -0.53814 | -0.01070 |
| C | 0.89429 | 1.33366 | -1.03490 |
| C | 1.61842 | -0.65213 | -2.42049 |
| Si | 3.80753 | -0.52123 | 0.05865 |
| C | 4.55184 | -1.96326 | -0.92334 |
| C | 4.49979 | 1.12388 | -0.58524 |
| C | 4.16598 | -0.75573 | 1.90214 |
| H | 4.21161 | 1.23838 | -1.63973 |
| H | 4.00461 | 1.94641 | -0.05077 |
| H | 5.25669 | -0.83149 | 2.02355 |
| H | 3.77117 | -1.73571 | 2.20663 |
| H | 5.63699 | -1.95425 | -0.73872 |
| H | 4.43799 | -1.76328 | -1.99778 |
| H | 2.53354 | -0.12879 | -2.71627 |
| H | 0.84712 | -0.42338 | -3.16377 |
| H | 1.80201 | -1.73092 | -2.43969 |
| H | 1.76831 | 1.83901 | -1.45888 |
| H | 0.06674 | 1.51084 | -1.73180 |
| H | 0.14455 | 1.18958 | 1.01712 |
| H | 1.48776 | 2.30714 | 0.82335 |
| H | -2.33607 | 4.71716 | -0.98708 |
| H | -2.37172 | 5.03550 | 0.74148 |
| H | -3.68903 | 4.11826 | -0.01115 |
| H | -0.93925 | -0.65675 | -1.41379 |
| C | 3.61351 | 0.33013 | 2.84090 |
| H | 4.00477 | 1.32413 | 2.59090 |
| H | 3.88094 | 0.12914 | 3.88682 |
| H | 2.51972 | 0.38381 | 2.79009 |
| C | 6.02730 | 1.27381 | -0.45749 |
| H | 6.56037 | 0.49995 | -1.02331 |
| H | 6.36510 | 2.24597 | -0.83976 |
| H | 6.35873 | 1.20384 | 0.58579 |
| C | 3.99157 | -3.35674 | -0.59098 |
| H | 2.91157 | -3.41430 | -0.77358 |
| H | 4.15763 | -3.61880 | 0.46121 |
| H | 4.46801 | -4.13718 | -1.19880 |

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Compound **5.30**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in methanol was used.

Electronic Energy: -1491.01566264 hartree.
Free Energy: -1490.484682 hartree.

| | | | |
|---|---|---|---|
| C | -0.52502 | -2.32163 | -0.59363 |
| C | 0.96539 | -2.43859 | -0.90532 |
| O | 1.32663 | -2.50307 | -2.08376 |
| C | 1.95585 | -2.46342 | 0.21587 |
| C | 3.23194 | -2.17060 | -0.11653 |
| C | 1.47172 | -2.70900 | 1.62498 |
| H | 3.42347 | -2.00290 | -1.17451 |
| C | 4.39421 | -1.94093 | 0.80437 |
| H | 4.29067 | -2.51908 | 1.72898 |
| C | 4.53081 | -0.44162 | 1.17565 |
| H | 5.31665 | -2.27820 | 0.31325 |
| H | 3.59240 | -0.12659 | 1.64537 |
| C | 4.87978 | 0.49037 | -0.01804 |
| H | 5.30646 | -0.34542 | 1.94659 |
| C | 6.38569 | 0.79139 | -0.05070 |
| C | 4.03235 | 1.77348 | 0.02281 |
| H | 4.61982 | -0.01488 | -0.95745 |
| H | 6.95524 | -0.14455 | -0.00402 |
| H | 6.68917 | 1.40575 | 0.80702 |
| H | 6.68557 | 1.31221 | -0.96613 |
| O | 2.64598 | 1.33811 | -0.20017 |
| C | 4.34686 | 2.81543 | -1.04188 |
| H | 4.08113 | 2.22599 | 1.01625 |
| H | 4.30948 | 2.38008 | -2.04745 |
| H | 5.34181 | 3.24357 | -0.88451 |
| H | 3.61852 | 3.63220 | -0.99023 |
| C | 1.67575 | 1.76945 | 0.62410 |
| O | 1.86996 | 2.51592 | 1.57831 |
| C | 0.33550 | 1.24208 | 0.29764 |
| C | 0.01397 | 0.60498 | -0.83695 |
| H | -0.40874 | 1.43507 | 1.06304 |
| C | -1.36358 | 0.07901 | -1.18378 |
| O | -2.19633 | 0.21700 | -0.02915 |
| C | -1.27600 | -1.41966 | -1.58935 |
| C | -1.89692 | 0.89278 | -2.37900 |
| Si | -3.86468 | 0.35594 | 0.22670 |
| C | -4.81480 | -1.04910 | -0.62616 |
| C | -4.01928 | 0.25061 | 2.11000 |
| C | -4.54070 | 2.02918 | -0.35891 |
| H | -3.44647 | 1.08302 | 2.54372 |
| H | -5.06899 | 0.45397 | 2.36951 |
| H | -5.60503 | 2.05434 | -0.07945 |
| H | -4.52860 | 2.06087 | -1.45694 |
| H | -4.36515 | -2.00728 | -0.33067 |
| H | -4.66620 | -0.97357 | -1.71278 |
| H | -2.85805 | 0.49303 | -2.72105 |
| H | -1.19589 | 0.84062 | -3.21883 |
| H | -2.02441 | 1.94460 | -2.10594 |
| H | -2.30296 | -1.77540 | -1.71238 |
| H | -0.79410 | -1.49578 | -2.56921 |
| H | -0.92148 | -3.34552 | -0.66216 |
| H | -0.69721 | -1.99627 | 0.43451 |
| H | 2.30334 | -2.93538 | 2.29774 |
| H | 0.77252 | -3.55239 | 1.66814 |
| H | 0.94851 | -1.83536 | 2.03511 |
| H | 0.77217 | 0.44806 | -1.60125 |
| C | -3.83972 | 3.27587 | 0.20775 |
| H | -3.90466 | 3.31205 | 1.30221 |
| H | -4.29209 | 4.20011 | -0.17534 |
| H | -2.77523 | 3.29971 | -0.05503 |
| C | -3.57097 | -1.06960 | 2.75816 |
| H | -2.50993 | -1.27026 | 2.56652 |
| H | -3.70731 | -1.04840 | 3.84753 |
| H | -4.14020 | -1.92618 | 2.37635 |
| C | -6.32500 | -1.07483 | -0.32327 |
| H | -6.52442 | -1.19010 | 0.74923 |
| H | -6.82073 | -1.90932 | -0.83633 |
| H | -6.82055 | -0.15314 | -0.65192 |

---

Compound **5.31**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -24.868172 kJ.

| | | | |
|---|---|---|---|
| C | 0.48980 | 2.67100 | -0.85800 |
| H | 0.21290 | 2.24660 | -1.81250 |
| C | -0.51150 | 2.96420 | 0.00100 |
| C | -0.31180 | 3.60530 | 1.36710 |
| H | -0.98020 | 4.45870 | 1.48180 |
| H | 0.69670 | 3.97030 | 1.53920 |
| H | -0.54650 | 2.89360 | 2.15800 |
| C | 1.99330 | 2.90720 | -0.72410 |
| H | 2.23030 | 3.42130 | 0.20270 |
| C | 2.76730 | 1.55280 | -0.75890 |
| H | 2.19140 | 0.84800 | -1.35900 |
| C | 2.40340 | 3.88790 | -1.84380 |
| H | 2.27590 | 3.45050 | -2.83450 |
| H | 3.44150 | 4.20690 | -1.74010 |
| H | 1.79660 | 4.79340 | -1.80480 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O | 4.00480 | 1.72600 | -1.42380 | C | -4.30210 | 1.94530 | -0.20000 |
| H | 3.83150 | 2.08270 | -2.28220 | H | -4.42790 | 1.84000 | -1.27780 |
| C | 3.13280 | 0.90320 | 0.61200 | H | -4.61490 | 2.95480 | 0.06950 |
| H | 4.08740 | 1.33780 | 0.91480 | H | -5.00750 | 1.26350 | 0.27610 |
| C | 2.17880 | 1.22380 | 1.78000 | O | -2.85370 | 1.79370 | 1.62050 |
| H | 2.40110 | 0.62370 | 2.66100 | H | -3.22690 | 0.98680 | 1.95020 |
| H | 1.14450 | 1.03660 | 1.51150 | C | -1.97020 | 2.78790 | -0.42850 |
| H | 2.26120 | 2.26360 | 2.09080 | H | -2.44730 | 3.75470 | -0.26250 |
| C | 3.36130 | -0.62560 | 0.45540 | H | -2.00010 | 2.65180 | -1.51030 |
| H | 3.83790 | -0.80030 | -0.51090 | | | | |
| C | 4.30610 | -1.21430 | 1.52240 | --- | | | |
| H | 3.86330 | -1.12800 | 2.51440 | | | | |
| H | 5.22680 | -0.63010 | 1.54580 | Compound **5.31** | | | |
| C | 4.67080 | -2.68150 | 1.25510 | This structure was assigned as incorrect. | | | |
| H | 5.13410 | -2.79850 | 0.27490 | | | | |
| H | 3.78910 | -3.32210 | 1.28630 | Molecular Mechanics (OPLS-2005), gas | | | |
| H | 5.37380 | -3.05020 | 2.00220 | phase. | | | |
| O | 2.12020 | -1.32480 | 0.54150 | Energy: -20.970623 kJ. | | | |
| C | 1.53820 | -1.86030 | -0.54460 | | | | |
| O | 1.94120 | -1.75780 | -1.70360 | C | 0.71980 | 2.16800 | 0.04480 |
| C | 0.25170 | -2.62380 | -0.20230 | H | 1.07830 | 1.51110 | 0.81810 |
| H | 0.30260 | -2.87870 | 0.85560 | C | -0.48960 | 2.74800 | 0.20470 |
| C | 0.19670 | -3.95010 | -0.98550 | C | -1.09240 | 3.70730 | -0.81020 |
| H | 0.06230 | -3.77700 | -2.05380 | H | -1.70360 | 3.16670 | -1.53170 |
| H | -0.63100 | -4.57120 | -0.64340 | H | -0.33550 | 4.25540 | -1.36780 |
| H | 1.11320 | -4.52630 | -0.85450 | H | -1.71670 | 4.44910 | -0.31120 |
| C | -1.02130 | -1.77440 | -0.44820 | C | 1.66740 | 2.31420 | -1.13480 |
| H | -1.07550 | -1.59750 | -1.52310 | H | 1.63660 | 3.36450 | -1.42230 |
| O | -2.14940 | -2.54810 | -0.04200 | C | 3.15260 | 2.02620 | -0.78410 |
| C | -1.11910 | -0.41720 | 0.29000 | H | 3.70980 | 2.49840 | -1.59550 |
| H | -0.29920 | 0.21200 | -0.04370 | C | 1.17110 | 1.51640 | -2.35240 |
| C | -2.44830 | 0.21910 | -0.18900 | H | 1.09180 | 0.45250 | -2.13440 |
| H | -2.42620 | 0.24270 | -1.27840 | H | 1.84540 | 1.63300 | -3.20130 |
| C | -1.01170 | -0.59970 | 1.82330 | H | 0.18540 | 1.85410 | -2.67200 |
| H | -0.10200 | -1.12570 | 2.10650 | O | 3.53290 | 2.74930 | 0.37010 |
| H | -1.85270 | -1.16750 | 2.22100 | H | 3.26110 | 3.64940 | 0.26880 |
| H | -0.97390 | 0.35400 | 2.34550 | C | 3.66960 | 0.54940 | -0.74640 |
| O | -3.49550 | -0.65920 | 0.21420 | H | 3.36580 | 0.09080 | -1.68680 |
| C | -3.40880 | -1.97730 | -0.24160 | C | 5.21000 | 0.54540 | -0.81850 |
| C | -3.81370 | -2.06840 | -1.72640 | H | 5.60220 | -0.46970 | -0.88450 |
| H | -3.13330 | -1.52200 | -2.37540 | H | 5.65340 | 1.01770 | 0.05820 |
| H | -4.81670 | -1.66240 | -1.85930 | H | 5.56820 | 1.08470 | -1.69530 |
| H | -3.81580 | -3.11220 | -2.04100 | C | 3.20060 | -0.42880 | 0.38080 |
| C | -4.37930 | -2.78470 | 0.62170 | H | 3.84890 | -1.30310 | 0.29820 |
| H | -4.36610 | -3.83260 | 0.32160 | C | 3.39430 | 0.05940 | 1.83240 |
| H | -5.39170 | -2.39450 | 0.51530 | H | 2.73410 | 0.89470 | 2.05550 |
| H | -4.08390 | -2.71640 | 1.66890 | H | 4.40670 | 0.44420 | 1.95280 |
| C | -2.84170 | 1.67230 | 0.22030 | C | 3.16690 | -1.04700 | 2.87260 |

| | | | |
|---|---|---|---|
| H | 3.83220 | -1.89340 | 2.70000 |
| H | 2.14070 | -1.41460 | 2.84320 |
| H | 3.35480 | -0.67560 | 3.88010 |
| O | 1.86700 | -0.91770 | 0.23130 |
| C | 1.61180 | -1.97590 | -0.56770 |
| O | 2.41070 | -2.42580 | -1.39110 |
| C | 0.22920 | -2.63460 | -0.33550 |
| H | 0.25960 | -3.05400 | 0.66740 |
| C | 0.03490 | -3.83150 | -1.29370 |
| H | -0.07650 | -3.49760 | -2.32570 |
| H | -0.85350 | -4.40610 | -1.03210 |
| H | 0.87830 | -4.52190 | -1.25390 |
| C | -0.96520 | -1.64390 | -0.43930 |
| H | -0.79880 | -1.06750 | -1.34980 |
| O | -2.20200 | -2.35130 | -0.56470 |
| C | -1.17540 | -0.68580 | 0.75320 |
| H | -0.28070 | -0.10610 | 0.91420 |
| C | -2.29830 | 0.27360 | 0.29640 |
| H | -2.01680 | 0.67250 | -0.67780 |
| C | -1.45240 | -1.43440 | 2.07790 |
| H | -0.65760 | -2.13600 | 2.32240 |
| H | -2.38650 | -1.99470 | 2.03950 |
| H | -1.50650 | -0.74860 | 2.92160 |
| O | -3.47800 | -0.50260 | 0.12020 |
| C | -3.35820 | -1.58250 | -0.76470 |
| C | -3.43060 | -1.09250 | -2.22470 |
| H | -2.60240 | -0.43630 | -2.48230 |
| H | -4.36150 | -0.54790 | -2.38330 |
| H | -3.40810 | -1.94870 | -2.89920 |
| C | -4.53670 | -2.50820 | -0.45940 |
| H | -4.51270 | -3.37610 | -1.11880 |
| H | -5.47860 | -1.97770 | -0.60010 |
| H | -4.47670 | -2.85140 | 0.57350 |
| C | -2.61050 | 1.53390 | 1.14670 |
| C | -3.77850 | 2.33750 | 0.54250 |
| H | -3.58720 | 2.63360 | -0.48590 |
| H | -3.97950 | 3.24140 | 1.11810 |
| H | -4.69910 | 1.75300 | 0.52720 |
| O | -3.09340 | 1.10740 | 2.39690 |
| H | -3.62430 | 0.34080 | 2.21930 |
| C | -1.35970 | 2.41910 | 1.42080 |
| H | -0.73200 | 1.91330 | 2.15640 |
| H | -1.65680 | 3.35070 | 1.90370 |

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Compound **5.31**
This structure was assigned as incorrect.

B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1391.17480260 hartree.
Free Energy: -1390.592707 hartree.

| | | | |
|---|---|---|---|
| C | 0.53140 | 2.95065 | 0.57333 |
| H | 0.33398 | 3.01103 | 1.64469 |
| C | -0.56169 | 2.87080 | -0.20927 |
| C | -0.54300 | 2.82269 | -1.71988 |
| H | -0.93797 | 3.76084 | -2.13642 |
| H | -1.18796 | 2.02372 | -2.10593 |
| H | 0.45761 | 2.65070 | -2.11603 |
| C | 2.02400 | 2.83834 | 0.25592 |
| H | 2.51926 | 3.00115 | 1.21789 |
| C | 2.34878 | 1.37506 | -0.18129 |
| H | 1.51292 | 0.77384 | 0.18908 |
| C | 2.59554 | 3.90742 | -0.69315 |
| H | 2.17603 | 3.84039 | -1.69743 |
| H | 3.68323 | 3.80134 | -0.78348 |
| H | 2.38510 | 4.90671 | -0.29640 |
| O | 2.38275 | 1.32149 | -1.60531 |
| H | 2.05964 | 0.43958 | -1.87052 |
| C | 3.62012 | 0.70665 | 0.41749 |
| H | 4.50108 | 1.19460 | -0.02394 |
| C | 3.69585 | 0.81110 | 1.94929 |
| H | 4.57088 | 0.28415 | 2.34159 |
| H | 2.80716 | 0.37722 | 2.42206 |
| H | 3.77939 | 1.84994 | 2.27891 |
| C | 3.67680 | -0.76726 | -0.06336 |
| H | 3.63452 | -0.78228 | -1.15371 |
| C | 4.89043 | -1.56986 | 0.40351 |
| H | 4.84325 | -1.71177 | 1.48897 |
| H | 5.78391 | -0.96403 | 0.20235 |
| C | 5.02050 | -2.93108 | -0.28814 |
| H | 5.10251 | -2.81963 | -1.37584 |
| H | 4.15159 | -3.56410 | -0.07919 |
| H | 5.91174 | -3.46234 | 0.06274 |
| O | 2.48293 | -1.48258 | 0.43034 |
| C | 1.45234 | -1.68146 | -0.40595 |
| O | 1.44358 | -1.33926 | -1.58036 |
| C | 0.27494 | -2.39756 | 0.24676 |
| H | 0.42134 | -2.40346 | 1.32984 |
| C | 0.23613 | -3.85280 | -0.26270 |
| H | 0.13512 | -3.87720 | -1.35276 |
| H | -0.61594 | -4.37350 | 0.17833 |
| H | 1.15419 | -4.38392 | 0.01119 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.01416 | -1.62817 | -0.12393 | H | 0.88185 | 2.13314 | -2.18417 |
| H | -0.98737 | -1.50939 | -1.21583 | C | 1.94214 | 2.78604 | 0.26794 |
| O | -2.13990 | -2.43209 | 0.24195 | H | 2.30558 | 2.92562 | 1.28969 |
| C | -1.17350 | -0.22893 | 0.51358 | C | 2.32659 | 1.34202 | -0.16150 |
| H | -0.34962 | 0.39725 | 0.16633 | H | 1.41045 | 0.75142 | -0.06588 |
| C | -2.45472 | 0.34588 | -0.11774 | C | 2.63388 | 3.85569 | -0.58689 |
| H | -2.29774 | 0.36036 | -1.20594 | H | 2.27688 | 3.83334 | -1.61943 |
| C | -1.17347 | -0.26159 | 2.04850 | H | 3.71868 | 3.70385 | -0.60328 |
| H | -0.18589 | -0.54058 | 2.43359 | H | 2.43406 | 4.84987 | -0.17442 |
| H | -1.89917 | -0.98828 | 2.42398 | O | 2.75996 | 1.33428 | -1.51729 |
| H | -1.43581 | 0.71386 | 2.46175 | H | 2.45848 | 0.48757 | -1.89199 |
| O | -3.55613 | -0.54040 | 0.17941 | C | 3.38687 | 0.61866 | 0.69719 |
| C | -3.39963 | -1.91584 | -0.18637 | H | 4.35812 | 1.09484 | 0.50128 |
| C | -3.59599 | -2.10053 | -1.69894 | C | 3.09451 | 0.65994 | 2.19729 |
| H | -2.86248 | -1.54684 | -2.29034 | H | 3.80085 | 0.03925 | 2.75585 |
| H | -4.59228 | -1.75085 | -1.98545 | H | 2.08359 | 0.30042 | 2.41645 |
| H | -3.50654 | -3.16045 | -1.95565 | H | 3.18306 | 1.67329 | 2.59587 |
| C | -4.45058 | -2.67784 | 0.61129 | C | 3.51662 | -0.82732 | 0.17754 |
| H | -4.38380 | -3.74764 | 0.39393 | H | 3.71090 | -0.80489 | -0.89791 |
| H | -5.45252 | -2.32320 | 0.35319 | C | 4.58811 | -1.67303 | 0.85003 |
| H | -4.28058 | -2.52280 | 1.68000 | H | 4.30587 | -1.86124 | 1.89113 |
| C | -2.98118 | 1.76506 | 0.28134 | H | 5.51605 | -1.08920 | 0.86596 |
| C | -4.03588 | 2.18246 | -0.76419 | C | 4.80969 | -2.99793 | 0.12649 |
| H | -3.57886 | 2.40162 | -1.73655 | H | 5.13003 | -2.83236 | -0.90797 |
| H | -4.55085 | 3.08217 | -0.41389 | H | 3.88913 | -3.59049 | 0.10494 |
| H | -4.77738 | 1.38931 | -0.90384 | H | 5.57913 | -3.59388 | 0.62589 |
| O | -3.62002 | 1.67742 | 1.56239 | O | 2.25763 | -1.53484 | 0.38710 |
| H | -4.13617 | 0.85230 | 1.53577 | C | 1.38793 | -1.66738 | -0.61529 |
| C | -1.92382 | 2.91244 | 0.46984 | O | 1.54678 | -1.20637 | -1.73153 |
| H | -1.77142 | 2.99012 | 1.54922 | C | 0.16120 | -2.46906 | -0.22500 |
| H | -2.43507 | 3.83957 | 0.17078 | H | 0.23093 | -2.72343 | 0.83544 |
| --- | | | | C | 0.11090 | -3.75175 | -1.06057 |
| | | | | H | 0.10815 | -3.51128 | -2.12807 |
| Compound **5.31** | | | | H | -0.80023 | -4.30546 | -0.82160 |
| This structure was assigned as incorrect. | | | | H | 0.97206 | -4.39370 | -0.85167 |
| M06-2X/6-31g(d) | | | | C | -1.11573 | -1.63445 | -0.44182 |
| SMD implicit solvation in THF was used. | | | | H | -1.29345 | -1.57173 | -1.52769 |
| | | | | O | -2.15495 | -2.37593 | 0.18513 |
| Electronic Energy: -1390.61679444 hartree. | | | | C | -1.07494 | -0.20746 | 0.12731 |
| | | | | H | -0.34892 | 0.34504 | -0.46924 |
| Free Energy: -1390.026496 hartree. | | | | C | -2.46417 | 0.39461 | -0.14430 |
| | | | | H | -2.63710 | 0.37811 | -1.23208 |
| C | 0.43094 | 2.99031 | 0.34329 | C | -0.65688 | -0.20227 | 1.59811 |
| H | 0.05785 | 3.34253 | 1.30625 | H | 0.28796 | -0.73570 | 1.73196 |
| C | -0.48732 | 2.76349 | -0.60684 | H | -1.41027 | -0.70260 | 2.21596 |
| C | -0.17428 | 2.34684 | -2.02236 | H | -0.52977 | 0.81726 | 1.96477 |
| H | -0.47654 | 3.14805 | -2.71049 | O | -3.42609 | -0.43833 | 0.51007 |
| H | -0.75626 | 1.46174 | -2.31466 | C | -3.44639 | -1.79520 | 0.09427 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.01487 | -1.93430 | -1.31732 | C | 3.74657 | 0.84827 | 1.91626 |
| H | -3.39778 | -1.44787 | -2.07640 | H | 4.62319 | 0.31379 | 2.29488 |
| H | -5.01504 | -1.49332 | -1.35462 | H | 2.86346 | 0.44094 | 2.42327 |
| H | -4.08721 | -2.99540 | -1.57208 | H | 3.85781 | 1.89188 | 2.22376 |
| C | -4.30167 | -2.52622 | 1.10991 | C | 3.68480 | -0.76265 | -0.07313 |
| H | -4.33631 | -3.59209 | 0.87131 | H | 3.64250 | -0.79393 | -1.16276 |
| H | -5.31853 | -2.12541 | 1.10323 | C | 4.89952 | -1.55858 | 0.39999 |
| H | -3.87083 | -2.39698 | 2.10624 | H | 4.85456 | -1.69311 | 1.48655 |
| C | -2.78855 | 1.83103 | 0.33003 | H | 5.78977 | -0.95059 | 0.19226 |
| C | -4.26929 | 2.11771 | 0.04117 | C | 5.03701 | -2.92199 | -0.28337 |
| H | -4.51164 | 1.93880 | -1.01220 | H | 5.11600 | -2.81713 | -1.37247 |
| H | -4.48782 | 3.16437 | 0.27588 | H | 4.17711 | -3.56634 | -0.06868 |
| H | -4.91220 | 1.48192 | 0.65395 | H | 5.93540 | -3.44167 | 0.06870 |
| O | -2.57298 | 1.95074 | 1.73278 | O | 2.48769 | -1.47315 | 0.42997 |
| H | -2.97634 | 1.16181 | 2.13319 | C | 1.45998 | -1.68948 | -0.40097 |
| C | -1.96781 | 2.95982 | -0.34126 | O | 1.45297 | -1.36692 | -1.58351 |
| H | -2.12344 | 3.82730 | 0.31097 | C | 0.28229 | -2.39998 | 0.25920 |
| H | -2.45764 | 3.19233 | -1.29491 | H | 0.43452 | -2.40230 | 1.34137 |
| --- | | | | C | 0.24324 | -3.85730 | -0.24294 |
| | | | | H | 0.10872 | -3.89371 | -1.32945 |
| Compound **5.31** | | | | H | -0.58732 | -4.38906 | 0.22642 |
| This structure was assigned as incorrect. | | | | H | 1.17331 | -4.37945 | 0.00711 |
| B3LYP/6-31g(d) | | | | C | -1.00933 | -1.63234 | -0.11200 |
| SMD implicit solvation in THF was used. | | | | H | -0.98439 | -1.51268 | -1.20284 |
| | | | | O | -2.13692 | -2.43745 | 0.25136 |
| Electronic Energy: -1391.19516329 hartree. | | | | C | -1.17450 | -0.23270 | 0.52366 |
| | | | | H | -0.35033 | 0.39364 | 0.17782 |
| Free Energy: -1390.615376 hartree. | | | | C | -2.45404 | 0.33944 | -0.11443 |
| | | | | H | -2.28881 | 0.35729 | -1.20007 |
| C | 0.52453 | 2.93926 | 0.58070 | C | -1.17495 | -0.26167 | 2.05750 |
| H | 0.33870 | 2.95436 | 1.65607 | H | -0.19088 | -0.54989 | 2.44458 |
| C | -0.57816 | 2.88685 | -0.19199 | H | -1.90775 | -0.97818 | 2.44029 |
| C | -0.57965 | 2.88585 | -1.70235 | H | -1.42332 | 0.71841 | 2.47022 |
| H | -0.98571 | 3.83270 | -2.08835 | O | -3.55659 | -0.54979 | 0.17491 |
| H | -1.22315 | 2.09298 | -2.10292 | C | -3.39490 | -1.92639 | -0.19385 |
| H | 0.41760 | 2.73369 | -2.11538 | C | -3.57479 | -2.10929 | -1.70727 |
| C | 2.01583 | 2.83865 | 0.25134 | H | -2.83922 | -1.55411 | -2.29530 |
| H | 2.51600 | 3.00355 | 1.20975 | H | -4.57080 | -1.76539 | -2.00390 |
| C | 2.34328 | 1.37540 | -0.18236 | H | -3.48223 | -3.16939 | -1.96433 |
| H | 1.52015 | 0.77221 | 0.21226 | C | -4.45370 | -2.69192 | 0.58862 |
| C | 2.57730 | 3.91032 | -0.69940 | H | -4.38232 | -3.76220 | 0.37207 |
| H | 2.15809 | 3.84549 | -1.70491 | H | -5.45459 | -2.34499 | 0.31465 |
| H | 3.66680 | 3.81595 | -0.78840 | H | -4.30602 | -2.53833 | 1.66165 |
| H | 2.36228 | 4.91006 | -0.30387 | C | -2.98705 | 1.75670 | 0.28404 |
| O | 2.33703 | 1.30945 | -1.61003 | C | -4.01871 | 2.18521 | -0.77766 |
| H | 2.04237 | 0.40996 | -1.84953 | H | -3.54342 | 2.41043 | -1.73942 |
| C | 3.63170 | 0.71792 | 0.38981 | H | -4.54059 | 3.08445 | -0.43393 |
| H | 4.50308 | 1.19775 | -0.07778 | H | -4.76067 | 1.39587 | -0.93942 |

| | | | |
|---|---|---|---|
| O | -3.66017 | 1.65789 | 1.55194 |
| H | -4.14731 | 0.81486 | 1.50923 |
| C | -1.93182 | 2.89787 | 0.50680 |
| H | -1.76008 | 2.93333 | 1.58574 |
| H | -2.45105 | 3.83388 | 0.25086 |

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Compound **5.31**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1391.18671036 hartree.
Free Energy: -1390.603720 hartree.

| | | | |
|---|---|---|---|
| C | 0.42554 | 2.79414 | -0.68472 |
| H | 0.30383 | 2.41537 | -1.70060 |
| C | -0.68792 | 3.06988 | 0.01593 |
| C | -0.70375 | 3.71376 | 1.38362 |
| H | -1.08561 | 4.74197 | 1.29872 |
| H | 0.28922 | 3.77119 | 1.83740 |
| H | -1.38070 | 3.19263 | 2.06532 |
| C | 1.86786 | 2.76147 | -0.22095 |
| H | 1.90308 | 2.94884 | 0.85656 |
| C | 2.32405 | 1.29683 | -0.46507 |
| H | 1.48365 | 0.69210 | -0.11193 |
| C | 2.76046 | 3.79301 | -0.93041 |
| H | 2.76154 | 3.62483 | -2.01077 |
| H | 3.79823 | 3.73079 | -0.57903 |
| H | 2.39934 | 4.80902 | -0.73749 |
| O | 2.48888 | 1.12188 | -1.87044 |
| H | 2.20366 | 0.21393 | -2.08416 |
| C | 3.56018 | 0.75304 | 0.29418 |
| H | 4.45760 | 1.20240 | -0.15392 |
| C | 3.53622 | 1.07327 | 1.79646 |
| H | 4.40064 | 0.64504 | 2.31350 |
| H | 2.63223 | 0.68205 | 2.27753 |
| H | 3.56540 | 2.15346 | 1.96635 |
| C | 3.67394 | -0.76722 | 0.00051 |
| H | 3.73784 | -0.90481 | -1.08065 |
| C | 4.84344 | -1.48281 | 0.67396 |
| H | 4.68950 | -1.49491 | 1.75886 |
| H | 5.74616 | -0.88539 | 0.48949 |
| C | 5.05603 | -2.91328 | 0.16764 |
| H | 5.24352 | -2.93045 | -0.91259 |
| H | 4.17793 | -3.53657 | 0.36703 |
| H | 5.91451 | -3.37857 | 0.66396 |
| O | 2.44750 | -1.45406 | 0.45264 |
| C | 1.49433 | -1.76263 | -0.44392 |
| O | 1.57069 | -1.53413 | -1.64262 |
| C | 0.29086 | -2.45367 | 0.18231 |
| H | 0.38652 | -2.41339 | 1.26981 |
| C | 0.27635 | -3.92888 | -0.26646 |
| H | 0.23264 | -3.99835 | -1.35841 |
| H | -0.59698 | -4.43113 | 0.15437 |
| H | 1.17803 | -4.44864 | 0.07536 |
| C | -1.00862 | -1.72630 | -0.24507 |
| H | -1.06437 | -1.79186 | -1.34188 |
| O | -2.08624 | -2.46200 | 0.34538 |
| C | -1.11860 | -0.23754 | 0.16742 |
| H | -0.36479 | 0.31859 | -0.39326 |
| C | -2.49213 | 0.24092 | -0.35074 |
| H | -2.49810 | 0.09332 | -1.44202 |
| C | -0.88918 | -0.04457 | 1.67379 |
| H | 0.14303 | -0.29409 | 1.94182 |
| H | -1.55128 | -0.69466 | 2.25348 |
| H | -1.07734 | 0.98443 | 1.97479 |
| O | -3.51205 | -0.58612 | 0.24810 |
| C | -3.39568 | -1.99373 | 0.02918 |
| C | -3.78618 | -2.36129 | -1.41064 |
| H | -3.12743 | -1.90779 | -2.15551 |
| H | -4.80751 | -2.02562 | -1.61360 |
| H | -3.73932 | -3.44705 | -1.53738 |
| C | -4.32409 | -2.64844 | 1.04462 |
| H | -4.26707 | -3.73713 | 0.95840 |
| H | -5.35656 | -2.33037 | 0.87385 |
| H | -4.02279 | -2.35750 | 2.05440 |
| C | -2.98854 | 1.70391 | -0.10824 |
| C | -4.33365 | 1.87048 | -0.85286 |
| H | -4.20800 | 1.79088 | -1.93945 |
| H | -4.75235 | 2.85483 | -0.62341 |
| H | -5.04609 | 1.10526 | -0.53496 |
| O | -3.21783 | 1.91475 | 1.28811 |
| H | -3.69272 | 1.12210 | 1.59352 |
| C | -2.04598 | 2.83283 | -0.62774 |
| H | -2.63886 | 3.75445 | -0.53775 |
| H | -1.90752 | 2.65925 | -1.70206 |

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Compound **5.31**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1390.62655856 hartree.
Free Energy: -1390.037617 hartree.

| | | | |
|---|---|---|---|
| C | 0.37675 | 2.75646 | -0.67925 |
| H | 0.29662 | 2.34636 | -1.68768 |
| C | -0.76076 | 3.05008 | -0.03633 |
| C | -0.82345 | 3.73780 | 1.30366 |
| H | -1.30205 | 4.71893 | 1.18198 |
| H | 0.16627 | 3.90530 | 1.73581 |
| H | -1.43832 | 3.17998 | 2.01420 |
| C | 1.78604 | 2.72689 | -0.13714 |
| H | 1.75452 | 2.85110 | 0.94976 |
| C | 2.27257 | 1.29539 | -0.43057 |
| H | 1.44524 | 0.65781 | -0.09760 |
| C | 2.70355 | 3.78951 | -0.74216 |
| H | 2.74950 | 3.68297 | -1.82985 |
| H | 3.72335 | 3.70219 | -0.34822 |
| H | 2.33573 | 4.79405 | -0.50950 |
| O | 2.44425 | 1.17692 | -1.83475 |
| H | 2.21270 | 0.26262 | -2.07240 |
| C | 3.51906 | 0.77797 | 0.30477 |
| H | 4.40337 | 1.25691 | -0.13755 |
| C | 3.47905 | 1.06872 | 1.80410 |
| H | 4.34622 | 0.64512 | 2.31878 |
| H | 2.57441 | 0.65555 | 2.26632 |
| H | 3.48944 | 2.14625 | 1.99111 |
| C | 3.65770 | -0.72660 | -0.00671 |
| H | 3.73959 | -0.85614 | -1.08944 |
| C | 4.82267 | -1.43210 | 0.66945 |
| H | 4.65505 | -1.45444 | 1.75152 |
| H | 5.72509 | -0.83437 | 0.49267 |
| C | 5.01640 | -2.85145 | 0.14436 |
| H | 5.22549 | -2.84835 | -0.93092 |
| H | 4.11839 | -3.45481 | 0.31331 |
| H | 5.85100 | -3.34703 | 0.64874 |
| O | 2.45101 | -1.42304 | 0.42921 |
| C | 1.50724 | -1.72212 | -0.46447 |
| O | 1.58147 | -1.47404 | -1.65499 |
| C | 0.31855 | -2.43540 | 0.14222 |
| H | 0.39871 | -2.39695 | 1.23127 |
| C | 0.33981 | -3.89806 | -0.31910 |
| H | 0.29413 | -3.95381 | -1.41130 |
| H | -0.52199 | -4.42434 | 0.09641 |
| H | 1.25078 | -4.40293 | 0.01624 |
| C | -0.99016 | -1.75093 | -0.29140 |
| H | -1.10275 | -1.90440 | -1.37573 |
| O | -2.01385 | -2.44523 | 0.41130 |
| C | -1.08357 | -0.23980 | 0.00645 |
| H | -0.38681 | 0.27075 | -0.66618 |
| C | -2.49989 | 0.19325 | -0.40506 |
| H | -2.60262 | 0.00888 | -1.48574 |
| C | -0.73180 | 0.05575 | 1.46368 |
| H | 0.30506 | -0.22745 | 1.67743 |
| H | -1.38072 | -0.51482 | 2.13673 |
| H | -0.84637 | 1.11393 | 1.69695 |
| O | -3.44413 | -0.61013 | 0.31147 |
| C | -3.33285 | -2.01224 | 0.13344 |
| C | -3.77579 | -2.42828 | -1.26824 |
| H | -3.14503 | -2.01055 | -2.05594 |
| H | -4.80297 | -2.09395 | -1.43974 |
| H | -3.74137 | -3.51831 | -1.34953 |
| C | -4.20951 | -2.63710 | 1.20055 |
| H | -4.14231 | -3.72676 | 1.14862 |
| H | -5.25040 | -2.33664 | 1.05569 |
| H | -3.87299 | -2.30476 | 2.18616 |
| C | -2.99295 | 1.64521 | -0.15062 |
| C | -4.36270 | 1.78532 | -0.83351 |
| H | -4.27128 | 1.73264 | -1.92393 |
| H | -4.80035 | 2.75162 | -0.56683 |
| H | -5.03909 | 0.99214 | -0.50386 |
| O | -3.15746 | 1.84938 | 1.24691 |
| H | -3.58150 | 1.03807 | 1.57566 |
| C | -2.08728 | 2.76659 | -0.71219 |
| H | -2.69934 | 3.67926 | -0.68079 |
| H | -1.91484 | 2.53838 | -1.77137 |

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Compound **5.31**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in THF was used.

Electronic Energy: -1391.20652215 hartree.
Free Energy: -1390.625017 hartree.

| | | | |
|---|---|---|---|
| C | 0.42968 | 2.79719 | -0.68996 |
| H | 0.29288 | 2.41604 | -1.70314 |
| C | -0.67861 | 3.07407 | 0.02020 |
| C | -0.67956 | 3.71064 | 1.39084 |
| H | -1.06766 | 4.73823 | 1.31978 |
| H | 0.31780 | 3.76889 | 1.83592 |
| H | -1.34499 | 3.18163 | 2.07862 |
| C | 1.87681 | 2.76147 | -0.23961 |
| H | 1.92564 | 2.96009 | 0.83477 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.32649 | 1.29302 | -0.47094 | H | -3.73550 | -3.42284 | -1.56493 |
| H | 1.48529 | 0.69632 | -0.10744 | C | -4.34515 | -2.65031 | 1.01696 |
| C | 2.76551 | 3.78462 | -0.96504 | H | -4.29039 | -3.73890 | 0.92165 |
| H | 2.74478 | 3.62670 | -2.04783 | H | -5.37639 | -2.33352 | 0.83415 |
| H | 3.80973 | 3.71199 | -0.63476 | H | -4.06362 | -2.37104 | 2.03655 |
| H | 2.42203 | 4.80575 | -0.76226 | C | -2.98575 | 1.70997 | -0.09581 |
| O | 2.47684 | 1.09865 | -1.88000 | C | -4.32764 | 1.88127 | -0.84306 |
| H | 2.21140 | 0.17754 | -2.06396 | H | -4.20163 | 1.79083 | -1.92871 |
| C | 3.56429 | 0.75131 | 0.28619 | H | -4.74197 | 2.87116 | -0.62603 |
| H | 4.46400 | 1.19139 | -0.16581 | H | -5.04831 | 1.12538 | -0.51973 |
| C | 3.54727 | 1.08728 | 1.78451 | O | -3.22261 | 1.91701 | 1.30360 |
| H | 4.41303 | 0.66029 | 2.30082 | H | -3.68024 | 1.11159 | 1.60453 |
| H | 2.64396 | 0.70767 | 2.27711 | C | -2.04293 | 2.84018 | -0.61260 |
| H | 3.58449 | 2.16935 | 1.94349 | H | -2.63236 | 3.76331 | -0.51395 |
| C | 3.67480 | -0.77246 | 0.00628 | H | -1.91327 | 2.66986 | -1.68814 |
| H | 3.74964 | -0.92302 | -1.07203 | ---------- | | | |
| C | 4.83501 | -1.48763 | 0.69483 | | | | |
| H | 4.67015 | -1.49932 | 1.77820 | Compound **5.32** | | | |
| H | 5.73947 | -0.89102 | 0.51829 | This structure was assigned as incorrect. | | | |
| C | 5.05369 | -2.91665 | 0.18951 | | | | |
| H | 5.26690 | -2.93115 | -0.88651 | Molecular Mechanics (OPLS-2005), gas phase. | | | |
| H | 4.17173 | -3.54233 | 0.36700 | | | | |
| H | 5.90055 | -3.38469 | 0.70435 | Energy: +27.530088 kJ. | | | |
| O | 2.43805 | -1.45113 | 0.45318 | | | | |
| C | 1.49223 | -1.76975 | -0.44284 | H | 5.31330 | 9.18300 | 6.16460 |
| O | 1.57807 | -1.55496 | -1.64604 | C | 6.05540 | 8.95950 | 5.39550 |
| C | 0.28505 | -2.45710 | 0.18169 | O | 7.33590 | 8.97320 | 6.02250 |
| H | 0.38488 | -2.42153 | 1.26888 | C | 7.49350 | 8.46850 | 7.25810 |
| C | 0.26882 | -3.93087 | -0.26941 | O | 6.59610 | 8.02230 | 7.97390 |
| H | 0.20258 | -4.00467 | -1.36029 | C | 8.95530 | 8.45370 | 7.70760 |
| H | -0.59188 | -4.44193 | 0.16791 | H | 9.12750 | 9.30100 | 8.37160 |
| H | 1.17881 | -4.44782 | 0.05477 | H | 9.57770 | 8.62930 | 6.83280 |
| C | -1.01459 | -1.72531 | -0.24100 | C | 9.37010 | 7.13220 | 8.40180 |
| H | -1.07617 | -1.78536 | -1.33692 | H | 8.86900 | 6.29540 | 7.91230 |
| O | -2.09554 | -2.45984 | 0.34772 | O | 8.87260 | 7.15540 | 9.73320 |
| C | -1.12092 | -0.23735 | 0.17677 | H | 7.92640 | 7.23540 | 9.70020 |
| H | -0.36510 | 0.31692 | -0.38293 | C | 10.91080 | 6.86390 | 8.42470 |
| C | -2.49252 | 0.24690 | -0.34167 | C | 11.63390 | 8.07930 | 9.06460 |
| H | -2.49622 | 0.10230 | -1.43163 | H | 11.20530 | 8.33790 | 10.03320 |
| C | -0.88776 | -0.04714 | 1.68196 | H | 11.57690 | 8.96700 | 8.43420 |
| H | 0.14175 | -0.30663 | 1.95130 | H | 12.69230 | 7.87430 | 9.23230 |
| H | -1.55529 | -0.68721 | 2.26713 | C | 11.23140 | 5.63240 | 9.30880 |
| H | -1.06296 | 0.98441 | 1.98478 | H | 12.25650 | 5.28540 | 9.16910 |
| O | -3.51523 | -0.58010 | 0.25493 | H | 11.12050 | 5.86990 | 10.36740 |
| C | -3.40366 | -1.98741 | 0.02048 | H | 10.56630 | 4.79380 | 9.11410 |
| C | -3.78009 | -2.33798 | -1.42569 | C | 11.52170 | 6.61480 | 7.00950 |
| H | -3.11627 | -1.87738 | -2.16198 | O | 12.70450 | 6.89700 | 6.81010 |
| H | -4.80088 | -2.00200 | -1.63369 | C | 10.68980 | 5.95040 | 5.87660 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 9.71790 | 6.43600 | 5.84040 | H | 5.85490 | 9.29420 | 2.32410 |
| C | 10.44790 | 4.45750 | 6.19510 | H | 6.47900 | 10.99940 | 4.76090 |
| H | 9.87220 | 4.31860 | 7.10670 | H | 8.90720 | 8.82630 | 1.04420 |
| H | 11.39070 | 3.91900 | 6.30120 | | | | |
| H | 9.87600 | 3.96170 | 5.41090 | --- | | | |
| C | 11.36060 | 6.11700 | 4.47370 | | | | |
| H | 12.36590 | 5.69560 | 4.54230 | Compound **5.32** | | | |
| O | 10.70000 | 5.33620 | 3.48720 | This structure was assigned as correct. | | | |
| H | 9.76470 | 5.51350 | 3.48790 | | | | |
| C | 11.49810 | 7.57190 | 3.93450 | Molecular Mechanics (OPLS-2005), gas | | | |
| H | 12.07400 | 8.14320 | 4.66300 | phase. | | | |
| C | 12.33210 | 7.58360 | 2.63780 | Energy: +35.354385 kJ. | | | |
| H | 11.78690 | 7.13150 | 1.80860 | | | | |
| H | 13.25850 | 7.02260 | 2.76430 | H | 5.83600 | 7.51930 | 5.15110 |
| H | 12.61340 | 8.59380 | 2.34330 | C | 6.63890 | 6.95270 | 4.67640 |
| C | 10.14370 | 8.29730 | 3.75600 | O | 7.58120 | 6.49900 | 5.64000 |
| H | 9.60520 | 8.28040 | 4.69770 | C | 7.48740 | 6.86350 | 6.93130 |
| H | 9.52710 | 7.74940 | 3.04330 | O | 6.61010 | 7.57650 | 7.41770 |
| C | 10.26840 | 9.77180 | 3.31900 | C | 8.62150 | 6.29240 | 7.78610 |
| H | 10.68210 | 9.82720 | 2.31220 | H | 8.44900 | 6.51940 | 8.83740 |
| H | 10.99220 | 10.27430 | 3.96170 | H | 8.54290 | 5.20890 | 7.69600 |
| C | 8.94750 | 10.56770 | 3.36620 | C | 10.03360 | 6.75010 | 7.33800 |
| H | 9.13000 | 11.58020 | 3.00420 | H | 10.01500 | 6.89660 | 6.25770 |
| H | 8.64490 | 10.67380 | 4.40620 | O | 10.88360 | 5.63580 | 7.55560 |
| C | 7.81990 | 9.96930 | 2.53050 | H | 11.50310 | 5.60970 | 6.82110 |
| C | 6.57050 | 9.75530 | 2.99000 | C | 10.60050 | 8.05390 | 8.01120 |
| C | 6.00490 | 10.10340 | 4.36080 | C | 9.49950 | 9.14430 | 8.09540 |
| C | 5.71160 | 7.58970 | 4.80380 | H | 9.88540 | 10.08080 | 8.50130 |
| C | 6.69220 | 6.73300 | 4.44190 | H | 8.67750 | 8.85170 | 8.74780 |
| H | 7.70330 | 7.08930 | 4.54120 | H | 9.08320 | 9.36820 | 7.11270 |
| C | 4.22290 | 7.30580 | 4.70310 | C | 11.06480 | 7.77600 | 9.46120 |
| H | 3.85180 | 6.88710 | 5.63900 | H | 10.24050 | 7.41770 | 10.07750 |
| H | 3.99150 | 6.62600 | 3.88520 | H | 11.45580 | 8.67810 | 9.93330 |
| H | 3.67330 | 8.22610 | 4.50420 | H | 11.84830 | 7.02020 | 9.51360 |
| C | 6.64260 | 5.35670 | 3.94340 | C | 11.79520 | 8.64660 | 7.20200 |
| C | 5.59920 | 4.46930 | 4.01110 | O | 11.78030 | 9.81690 | 6.81020 |
| C | 7.62090 | 3.59160 | 2.91490 | C | 13.05000 | 7.78740 | 6.93590 |
| H | 4.62620 | 4.59460 | 4.45820 | H | 13.01530 | 6.94720 | 7.62690 |
| C | 8.69180 | 2.81600 | 2.23090 | C | 14.31360 | 8.58220 | 7.32470 |
| H | 9.51610 | 2.63310 | 2.92040 | H | 14.21960 | 9.00910 | 8.32410 |
| H | 9.07160 | 3.37710 | 1.37700 | H | 14.50060 | 9.40520 | 6.63410 |
| H | 8.30540 | 1.85940 | 1.88040 | H | 15.19580 | 7.94230 | 7.32890 |
| S | 6.02380 | 2.94330 | 3.28180 | C | 13.18660 | 7.20090 | 5.49530 |
| N | 7.78250 | 4.85310 | 3.32040 | H | 14.22100 | 6.85900 | 5.43140 |
| C | 8.17780 | 9.63440 | 1.09250 | O | 12.42430 | 6.02020 | 5.32890 |
| H | 8.60220 | 10.50770 | 0.59680 | H | 12.59730 | 5.68700 | 4.45780 |
| H | 7.30330 | 9.31990 | 0.52240 | C | 12.94420 | 8.15410 | 4.28710 |
| H | 4.96400 | 10.38390 | 4.19940 | H | 13.29540 | 9.14310 | 4.58630 |

| | | | |
|---|---|---|---|
| C | 13.81180 | 7.72660 | 3.08770 |
| H | 14.86640 | 7.67340 | 3.36020 |
| H | 13.51720 | 6.74940 | 2.70490 |
| H | 13.73890 | 8.43810 | 2.26580 |
| C | 11.45750 | 8.28410 | 3.86010 |
| H | 10.82290 | 8.34200 | 4.73820 |
| H | 11.13370 | 7.38600 | 3.33310 |
| C | 11.16650 | 9.52680 | 2.99870 |
| H | 11.70330 | 9.45090 | 2.05350 |
| H | 11.56200 | 10.41540 | 3.49160 |
| C | 9.67140 | 9.73050 | 2.68810 |
| H | 9.30170 | 8.88370 | 2.11280 |
| H | 9.56290 | 10.59070 | 2.02640 |
| C | 8.80630 | 9.99150 | 3.91890 |
| C | 7.80050 | 9.19010 | 4.32370 |
| C | 7.35230 | 7.88830 | 3.68070 |
| C | 5.99630 | 5.76320 | 3.97490 |
| C | 4.65640 | 5.72280 | 3.80930 |
| H | 4.08910 | 6.57610 | 4.15290 |
| C | 6.96070 | 4.67000 | 3.53060 |
| H | 6.57000 | 4.08970 | 2.69650 |
| H | 7.18050 | 3.99960 | 4.36180 |
| H | 7.90370 | 5.09810 | 3.19240 |
| C | 3.81770 | 4.65400 | 3.24820 |
| C | 4.09900 | 3.31120 | 3.23450 |
| C | 1.98090 | 3.91750 | 2.14480 |
| H | 4.94770 | 2.79610 | 3.65590 |
| C | 0.67460 | 3.99560 | 1.43570 |
| H | -0.08880 | 4.39040 | 2.10620 |
| H | 0.36740 | 3.00660 | 1.09570 |
| H | 0.75950 | 4.65420 | 0.57120 |
| S | 2.84100 | 2.40750 | 2.43660 |
| N | 2.61700 | 4.98970 | 2.62260 |
| C | 9.12650 | 11.26960 | 4.67190 |
| H | 10.12010 | 11.21670 | 5.11700 |
| H | 8.41690 | 11.45090 | 5.47960 |
| H | 8.20220 | 7.37570 | 3.23330 |
| H | 7.22200 | 9.48980 | 5.18690 |
| H | 6.66680 | 8.14050 | 2.87110 |
| H | 9.09590 | 12.12720 | 3.99970 |

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Compound **5.32**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1882.64137213 hartree.
Free Energy: -1882.063230 hartree.

| | | | |
|---|---|---|---|
| H | -1.95325 | 1.84434 | 1.40101 |
| C | -1.61139 | 1.55801 | 0.40449 |
| O | -0.39832 | 0.75038 | 0.56311 |
| C | -0.33115 | -0.07334 | 1.62980 |
| O | -1.15424 | -0.10338 | 2.52244 |
| C | 0.90294 | -0.95696 | 1.57945 |
| H | 0.88859 | -1.57304 | 2.48240 |
| H | 1.79904 | -0.32589 | 1.61635 |
| C | 0.91992 | -1.82656 | 0.30862 |
| H | 1.04712 | -1.17205 | -0.55749 |
| O | -0.35988 | -2.42800 | 0.10529 |
| H | -0.60479 | -2.90569 | 0.91770 |
| C | 2.05706 | -2.91612 | 0.27450 |
| C | 1.84756 | -3.97124 | 1.37486 |
| H | 0.88118 | -4.47094 | 1.24617 |
| H | 1.89183 | -3.54676 | 2.38082 |
| H | 2.62359 | -4.74058 | 1.31374 |
| C | 1.99072 | -3.61227 | -1.10494 |
| H | 2.72796 | -4.41876 | -1.17528 |
| H | 0.99575 | -4.04739 | -1.23490 |
| H | 2.15827 | -2.91517 | -1.93220 |
| C | 3.42976 | -2.23837 | 0.47204 |
| O | 4.07568 | -2.45930 | 1.49410 |
| C | 4.03139 | -1.31590 | -0.59916 |
| H | 3.23607 | -0.96569 | -1.26592 |
| C | 5.03754 | -2.16298 | -1.41711 |
| H | 4.59156 | -3.10478 | -1.74907 |
| H | 5.91460 | -2.39742 | -0.80816 |
| H | 5.37036 | -1.62599 | -2.30704 |
| C | 4.67741 | -0.08474 | 0.11546 |
| H | 3.93733 | 0.25953 | 0.85501 |
| O | 5.86607 | -0.46592 | 0.80930 |
| H | 5.59346 | -1.22667 | 1.35905 |
| C | 5.03099 | 1.15893 | -0.73293 |
| H | 5.51291 | 1.82260 | 0.00087 |
| C | 6.06202 | 0.92270 | -1.84764 |
| H | 6.89502 | 0.30479 | -1.49850 |
| H | 6.47408 | 1.88347 | -2.18029 |
| H | 5.61980 | 0.44224 | -2.72803 |
| C | 3.80077 | 1.91627 | -1.27654 |
| H | 3.22002 | 1.26575 | -1.94706 |
| H | 4.17469 | 2.73439 | -1.90860 |
| C | 2.87753 | 2.51736 | -0.20482 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 3.49228 | 3.03246 | 0.54541 | O | 0.36056 | -0.28767 | 3.52427 |
| H | 2.33407 | 1.72731 | 0.32711 | C | 2.12388 | 0.18874 | 1.94945 |
| C | 1.84412 | 3.50331 | -0.79071 | H | 2.17847 | 0.72308 | 1.00047 |
| H | 1.26487 | 2.98724 | -1.56397 | H | 2.84201 | 0.65519 | 2.63411 |
| H | 2.38635 | 4.31565 | -1.29756 | C | 2.48375 | -1.30729 | 1.80833 |
| C | 0.93039 | 4.10281 | 0.25996 | H | 1.62018 | -1.83990 | 1.38555 |
| C | -0.36324 | 3.77559 | 0.41975 | O | 2.76347 | -1.85095 | 3.09762 |
| C | -1.19744 | 2.81362 | -0.38593 | H | 1.98612 | -1.62179 | 3.64221 |
| C | -2.68018 | 0.72844 | -0.28238 | C | 3.70296 | -1.55623 | 0.88534 |
| C | -3.90312 | 0.68215 | 0.28470 | C | 4.91902 | -0.71774 | 1.33051 |
| H | -4.05988 | 1.24105 | 1.20551 | H | 5.11990 | -0.89687 | 2.39121 |
| C | -2.29515 | 0.03139 | -1.56204 | H | 4.75687 | 0.35563 | 1.18520 |
| H | -2.02847 | -1.01639 | -1.37268 | H | 5.80535 | -0.99665 | 0.75548 |
| H | -1.42322 | 0.50002 | -2.02827 | C | 4.09873 | -3.05539 | 0.96012 |
| H | -3.11461 | 0.04441 | -2.28940 | H | 4.87264 | -3.27917 | 0.21848 |
| C | -5.11372 | -0.00411 | -0.16764 | H | 4.49583 | -3.27858 | 1.95397 |
| C | -5.25064 | -1.03389 | -1.06887 | H | 3.24820 | -3.72093 | 0.78428 |
| C | -7.33753 | -0.26214 | -0.02652 | C | 3.40337 | -1.23662 | -0.61229 |
| H | -4.48754 | -1.56860 | -1.61435 | O | 4.34936 | -1.02155 | -1.35635 |
| C | -8.75333 | -0.03367 | 0.40187 | C | 1.98064 | -1.29551 | -1.19459 |
| H | -8.76918 | 0.74585 | 1.16818 | H | 1.25984 | -0.91353 | -0.46649 |
| H | -9.19982 | -0.94460 | 0.81686 | C | 1.63120 | -2.78086 | -1.46296 |
| H | -9.37849 | 0.28894 | -0.43908 | H | 2.38043 | -3.24559 | -2.11493 |
| S | -6.91388 | -1.50110 | -1.21276 | H | 0.66010 | -2.84379 | -1.95791 |
| N | -6.31432 | 0.40731 | 0.41165 | H | 1.57988 | -3.35609 | -0.53488 |
| C | 1.57269 | 5.12538 | 1.17035 | C | 1.85213 | -0.46875 | -2.49549 |
| H | 2.41844 | 4.69960 | 1.72667 | H | 2.58583 | -0.87104 | -3.20790 |
| H | 0.86015 | 5.52597 | 1.89919 | O | 0.52618 | -0.72774 | -2.99226 |
| H | -0.69666 | 2.50916 | -1.30910 | H | 0.45176 | -0.30479 | -3.86385 |
| H | -0.90790 | 4.26416 | 1.23032 | C | 2.10994 | 1.05827 | -2.37295 |
| H | -2.13027 | 3.31378 | -0.67978 | H | 3.07654 | 1.17532 | -1.86565 |
| H | 1.97719 | 5.96794 | 0.59142 | C | 2.26020 | 1.66840 | -3.77881 |
| ---------- | | | | H | 2.56369 | 2.71910 | -3.73130 |
| | | | | H | 1.31688 | 1.63155 | -4.34176 |
| Compound **5.32** | | | | H | 3.02014 | 1.13333 | -4.36149 |
| This structure was assigned as incorrect. | | | | C | 1.02965 | 1.78440 | -1.54322 |
| B3LYP/6-31g(d) | | | | H | 0.05681 | 1.64227 | -2.02922 |
| SMD implicit solvation in dichloromethane was used. | | | | H | 0.94361 | 1.30704 | -0.56197 |
| | | | | C | 1.29011 | 3.28624 | -1.33305 |
| | | | | H | 1.13856 | 3.82706 | -2.27506 |
| Electronic Energy: -1882.63674595 hartree. | | | | H | 2.34509 | 3.43973 | -1.06414 |
| | | | | C | 0.43275 | 3.94065 | -0.22144 |
| Free Energy: -1882.058075 hartree. | | | | H | 0.67350 | 5.01591 | -0.21466 |
| | | | | H | 0.74850 | 3.54115 | 0.74631 |
| H | -1.29282 | 1.46150 | 3.47960 | C | -1.06741 | 3.78314 | -0.38090 |
| C | -1.32707 | 1.55355 | 2.38998 | C | -1.89476 | 3.36476 | 0.59436 |
| O | 0.00902 | 1.24992 | 1.89446 | C | -1.57566 | 3.04094 | 2.03682 |
| C | 0.74841 | 0.34384 | 2.55249 | C | -2.37295 | 0.59069 | 1.84825 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.15793 | -0.04052 | 0.67615 | C | -3.32353 | -2.68275 | -2.02313 |
| H | -1.21414 | 0.16146 | 0.17680 | H | -3.63458 | -2.44782 | -3.04730 |
| C | -3.60241 | 0.49697 | 2.71298 | H | -4.21096 | -2.94436 | -1.44378 |
| H | -3.33783 | 0.11739 | 3.71019 | H | -2.65847 | -3.55169 | -2.05974 |
| H | -4.04771 | 1.49021 | 2.86697 | C | -1.37728 | -1.13555 | -2.28235 |
| H | -4.35672 | -0.15835 | 2.27900 | H | -0.75480 | -2.01977 | -2.44544 |
| C | -2.99507 | -0.96827 | -0.08333 | H | -1.70936 | -0.77874 | -3.26275 |
| C | -2.61135 | -1.44446 | -1.31583 | H | -0.73699 | -0.36561 | -1.84426 |
| C | -4.78452 | -2.24504 | -0.50395 | C | -2.26179 | -1.82520 | 0.04153 |
| H | -1.70465 | -1.21800 | -1.86565 | O | -3.18055 | -1.97584 | 0.83635 |
| C | -6.11088 | -2.91134 | -0.31217 | C | -0.83193 | -2.08415 | 0.46501 |
| H | -6.01107 | -4.00303 | -0.29569 | H | -0.18107 | -1.35745 | -0.03486 |
| H | -6.80835 | -2.65472 | -1.11789 | C | -0.44256 | -3.49161 | -0.03409 |
| H | -6.53808 | -2.58447 | 0.63950 | H | -0.48728 | -3.58167 | -1.12169 |
| S | -3.81636 | -2.50691 | -1.96089 | H | -1.11229 | -4.24222 | 0.40035 |
| N | -4.22958 | -1.43933 | 0.35141 | H | 0.57818 | -3.71216 | 0.28869 |
| C | -1.63383 | 4.18309 | -1.72510 | C | -0.58399 | -2.00954 | 1.98612 |
| H | -2.72593 | 4.10555 | -1.74141 | H | -1.07972 | -2.87575 | 2.44494 |
| H | -1.24055 | 3.56265 | -2.54049 | O | 0.80802 | -2.18988 | 2.22012 |
| H | -2.42300 | 3.36665 | 2.65297 | H | 1.30149 | -1.65997 | 1.56067 |
| H | -2.95324 | 3.29068 | 0.34272 | C | -1.09551 | -0.75685 | 2.72332 |
| H | -0.70468 | 3.59938 | 2.39635 | H | -2.18543 | -0.73073 | 2.60185 |
| H | -1.36532 | 5.22145 | -1.96873 | C | -0.78522 | -0.90441 | 4.21513 |
| ---------- | | | | H | -1.28649 | -0.13361 | 4.80788 |
| | | | | H | 0.29293 | -0.83221 | 4.39435 |
| Compound **5.32** | | | | H | -1.12176 | -1.87852 | 4.58831 |
| This structure was assigned as incorrect. | | | | C | -0.51911 | 0.54110 | 2.14954 |
| M06-2X/6-31g(d) | | | | H | 0.58037 | 0.48515 | 2.15510 |
| SMD implicit solvation in dichloromethane was used. | | | | H | -0.81454 | 0.63861 | 1.09800 |
| | | | | C | -0.97389 | 1.79687 | 2.89888 |
| | | | | H | -0.53393 | 1.80814 | 3.90323 |
| Electronic Energy: -1881.98668443 hartree. | | | | H | -2.06246 | 1.75627 | 3.04268 |
| | | | | C | -0.63154 | 3.11275 | 2.17936 |
| Free Energy: -1881.396331 hartree. | | | | H | -0.93129 | 3.94434 | 2.83373 |
| | | | | H | -1.22530 | 3.18621 | 1.26438 |
| H | -0.17751 | 3.10239 | -2.46244 | C | 0.83848 | 3.25241 | 1.85858 |
| C | 0.18829 | 2.72627 | -1.50355 | C | 1.31886 | 3.57716 | 0.65103 |
| O | -0.89055 | 2.01847 | -0.86555 | C | 0.54524 | 3.92150 | -0.59779 |
| C | -1.97996 | 1.71420 | -1.59623 | C | 1.37077 | 1.81030 | -1.73697 |
| O | -2.10718 | 1.98203 | -2.76777 | C | 1.53113 | 0.73033 | -0.95760 |
| C | -3.03679 | 1.01866 | -0.77123 | H | 0.78433 | 0.54660 | -0.19251 |
| H | -2.67723 | 0.82252 | 0.24364 | C | 2.34369 | 2.26633 | -2.78856 |
| H | -3.87758 | 1.71725 | -0.69613 | H | 2.03661 | 3.22209 | -3.22291 |
| C | -3.58812 | -0.26057 | -1.43073 | H | 2.41211 | 1.53897 | -3.60702 |
| H | -3.78851 | -0.03185 | -2.48453 | H | 3.35067 | 2.39143 | -2.37239 |
| O | -4.83330 | -0.58498 | -0.85189 | C | 2.60179 | -0.26382 | -0.96388 |
| H | -4.63247 | -1.04439 | -0.01585 | C | 3.67428 | -0.39443 | -1.80393 |
| C | -2.59939 | -1.46504 | -1.41943 | C | 3.50846 | -2.10401 | -0.06511 |

| | | | |
|---|---|---|---|
| H | 3.96107 | 0.21590 | -2.64697 |
| C | 3.69606 | -3.27156 | 0.85001 |
| H | 2.87946 | -3.29022 | 1.57558 |
| H | 4.64766 | -3.19959 | 1.38523 |
| H | 3.69450 | -4.21086 | 0.28860 |
| S | 4.61429 | -1.77152 | -1.36962 |
| N | 2.53391 | -1.25008 | 0.01849 |
| C | 1.78016 | 3.02221 | 3.01403 |
| H | 2.81632 | 3.23244 | 2.73441 |
| H | 1.73016 | 1.98893 | 3.37855 |
| H | 1.14902 | 4.60943 | -1.20063 |
| H | 2.40319 | 3.62509 | 0.54519 |
| H | -0.39060 | 4.44292 | -0.36941 |
| H | 1.51556 | 3.66739 | 3.86203 |

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Compound **5.32**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1882.60701546 hartree.
Free Energy: -1882.026070 hartree.

| | | | |
|---|---|---|---|
| H | -1.47993 | -3.28659 | -2.03949 |
| C | -1.49767 | -2.69273 | -1.11826 |
| O | -0.13123 | -2.31605 | -0.82743 |
| C | 0.68157 | -2.00706 | -1.86081 |
| O | 0.31933 | -1.97889 | -3.02432 |
| C | 2.07983 | -1.67736 | -1.39924 |
| H | 2.76228 | -2.40906 | -1.84621 |
| H | 2.15498 | -1.75550 | -0.31543 |
| C | 2.47733 | -0.27275 | -1.91388 |
| H | 1.66084 | 0.42724 | -1.69019 |
| O | 2.70186 | -0.32660 | -3.31856 |
| H | 1.91562 | -0.76516 | -3.69431 |
| C | 3.76756 | 0.29434 | -1.23909 |
| C | 4.93527 | -0.70603 | -1.35350 |
| H | 5.87211 | -0.23844 | -1.02881 |
| H | 5.05020 | -1.01637 | -2.39608 |
| H | 4.77489 | -1.58649 | -0.72824 |
| C | 4.15139 | 1.60091 | -1.96662 |
| H | 4.51409 | 1.36317 | -2.96908 |
| H | 4.94759 | 2.13145 | -1.43038 |
| H | 3.29841 | 2.27651 | -2.08248 |
| C | 3.44821 | 0.52689 | 0.26772 |
| O | 3.61297 | -0.38235 | 1.06749 |
| C | 2.95487 | 1.88960 | 0.78786 |
| H | 2.95621 | 2.61076 | -0.03141 |
| C | 3.92391 | 2.39255 | 1.87381 |
| H | 4.02662 | 1.66606 | 2.68434 |
| H | 3.57198 | 3.34194 | 2.29392 |
| H | 4.92203 | 2.56403 | 1.45504 |
| C | 1.47856 | 1.87196 | 1.27557 |
| H | 1.29092 | 2.90720 | 1.60873 |
| O | 0.70252 | 1.62004 | 0.10682 |
| H | -0.24264 | 1.84599 | 0.24077 |
| C | 1.14723 | 0.92843 | 2.48378 |
| H | 2.09603 | 0.64211 | 2.95097 |
| C | 0.31481 | 1.69318 | 3.52830 |
| H | 0.85775 | 2.56452 | 3.91457 |
| H | -0.62610 | 2.05361 | 3.08988 |
| H | 0.05804 | 1.06081 | 4.38562 |
| C | 0.43544 | -0.36905 | 2.04815 |
| H | 0.85297 | -0.71778 | 1.10305 |
| H | -0.61930 | -0.14640 | 1.83966 |
| C | 0.52526 | -1.51771 | 3.06180 |
| H | 1.58009 | -1.79006 | 3.19795 |
| H | 0.16470 | -1.19497 | 4.04725 |
| C | -0.24656 | -2.78778 | 2.62438 |
| H | -0.10256 | -3.55190 | 3.40470 |
| H | 0.20825 | -3.17913 | 1.70953 |
| C | -1.73499 | -2.58022 | 2.42393 |
| C | -2.41840 | -2.91505 | 1.31660 |
| C | -1.93618 | -3.60630 | 0.06138 |
| C | -2.40568 | -1.49339 | -1.32508 |
| C | -2.02234 | -0.27168 | -0.91331 |
| H | -1.04013 | -0.17572 | -0.46634 |
| C | -3.73824 | -1.81528 | -1.95587 |
| H | -3.80927 | -1.39572 | -2.96864 |
| H | -4.57230 | -1.40846 | -1.37068 |
| H | -3.89258 | -2.89514 | -2.04736 |
| C | -2.75023 | 0.99352 | -0.94688 |
| C | -3.93816 | 1.32384 | -1.55557 |
| C | -2.86629 | 3.15240 | -0.32419 |
| H | -4.57761 | 0.71053 | -2.16985 |
| C | -2.48496 | 4.44663 | 0.32777 |
| H | -3.20609 | 4.73153 | 1.10262 |
| H | -2.43783 | 5.26416 | -0.39996 |
| H | -1.50211 | 4.33524 | 0.79179 |
| S | -4.34080 | 2.98383 | -1.26413 |
| N | -2.16607 | 2.05872 | -0.25623 |
| C | -2.47206 | -1.97150 | 3.59655 |
| H | -2.28726 | -2.54512 | 4.51577 |
| H | -3.55265 | -1.94581 | 3.42506 |

| | | | |
|---|---|---|---|
| H | -2.75163 | -4.24135 | -0.30809 |
| H | -3.48592 | -2.69153 | 1.31681 |
| H | -1.09578 | -4.27890 | 0.26235 |
| H | -2.14028 | -0.94503 | 3.79841 |

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Compound **5.32**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1882.60379978 hartree.
Free Energy: -1882.027371 hartree.

| | | | |
|---|---|---|---|
| H | -1.66028 | 2.40926 | 1.43194 |
| C | -1.29936 | 2.07866 | 0.45522 |
| O | -0.12406 | 1.23407 | 0.70187 |
| C | -0.14908 | 0.47011 | 1.82164 |
| O | -1.09891 | 0.39335 | 2.57205 |
| C | 1.16604 | -0.24909 | 2.05869 |
| H | 1.89291 | 0.01850 | 1.28853 |
| H | 1.54106 | 0.12618 | 3.01682 |
| C | 1.03351 | -1.78995 | 2.24060 |
| H | 0.02982 | -1.98583 | 2.63508 |
| O | 1.92996 | -2.25062 | 3.23346 |
| H | 2.79522 | -2.35629 | 2.79108 |
| C | 1.16616 | -2.59731 | 0.89783 |
| C | 1.02275 | -4.10466 | 1.22876 |
| H | 0.04283 | -4.28438 | 1.68560 |
| H | 1.79067 | -4.42610 | 1.93408 |
| H | 1.09048 | -4.71903 | 0.32441 |
| C | 0.03840 | -2.18050 | -0.06153 |
| H | 0.02638 | -2.79791 | -0.96539 |
| H | -0.93073 | -2.31011 | 0.43327 |
| H | 0.10970 | -1.13405 | -0.36933 |
| C | 2.59197 | -2.38512 | 0.32562 |
| O | 3.55661 | -2.52549 | 1.07448 |
| C | 2.83500 | -2.08409 | -1.15343 |
| H | 2.02644 | -1.45692 | -1.54033 |
| C | 2.79754 | -3.42808 | -1.92626 |
| H | 1.82990 | -3.92916 | -1.82912 |
| H | 3.57258 | -4.10553 | -1.54993 |
| H | 2.98759 | -3.23728 | -2.98381 |
| C | 4.18664 | -1.37233 | -1.39113 |
| H | 4.97106 | -2.03861 | -1.00302 |
| O | 4.31114 | -1.25185 | -2.81442 |
| H | 5.21653 | -0.96492 | -3.00561 |
| C | 4.35706 | 0.00438 | -0.69708 |
| H | 4.11384 | -0.14616 | 0.36220 |
| C | 5.83206 | 0.44144 | -0.75718 |
| H | 6.16262 | 0.60570 | -1.79262 |
| H | 6.48825 | -0.31233 | -0.30628 |
| H | 5.99463 | 1.38213 | -0.22162 |
| C | 3.42039 | 1.08902 | -1.27116 |
| H | 2.42924 | 0.65870 | -1.46449 |
| H | 3.79607 | 1.41377 | -2.25061 |
| C | 3.22138 | 2.30143 | -0.34888 |
| H | 4.18453 | 2.76966 | -0.11026 |
| H | 2.80350 | 1.95443 | 0.60393 |
| C | 2.25961 | 3.35292 | -0.95734 |
| H | 2.82609 | 4.00669 | -1.63727 |
| H | 1.52675 | 2.82879 | -1.57710 |
| C | 1.55638 | 4.19194 | 0.08908 |
| C | 0.23904 | 4.12444 | 0.34355 |
| C | -0.79506 | 3.28337 | -0.35974 |
| C | -2.38710 | 1.28419 | -0.24979 |
| C | -3.50326 | 0.99953 | 0.45256 |
| H | -3.52509 | 1.32794 | 1.48929 |
| C | -2.11889 | 0.88846 | -1.68052 |
| H | -2.23390 | 1.74737 | -2.35652 |
| H | -1.08748 | 0.53330 | -1.79489 |
| H | -2.80799 | 0.11547 | -2.01729 |
| C | -4.71528 | 0.28326 | 0.06229 |
| C | -5.74426 | 0.05159 | 0.94583 |
| C | -6.08679 | -0.81893 | -1.31341 |
| H | -5.79996 | 0.33919 | 1.98669 |
| C | -6.60194 | -1.45973 | -2.56641 |
| H | -5.85430 | -1.33728 | -3.35350 |
| H | -7.53977 | -0.99900 | -2.89738 |
| H | -6.79024 | -2.52995 | -2.42290 |
| S | -7.02853 | -0.81853 | 0.18258 |
| N | -4.93954 | -0.22109 | -1.21272 |
| C | 2.44469 | 5.12413 | 0.87925 |
| H | 3.23311 | 4.57487 | 1.41111 |
| H | 1.87754 | 5.69783 | 1.61909 |
| H | -0.42501 | 2.92684 | -1.32414 |
| H | -0.15156 | 4.75156 | 1.14708 |
| H | -1.67875 | 3.90034 | -0.57628 |
| H | 2.95554 | 5.83615 | 0.21550 |

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Compound **5.32**
This structure was assigned as correct.
M06-2X/6-31g(d)

SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1881.97935541 hartree.
Free Energy: -1881.394165 hartree.

| | | | |
|---|---|---|---|
| H | 1.85873 | -0.02620 | -2.06832 |
| C | 1.64328 | 0.39945 | -1.08535 |
| O | 0.66775 | -0.45086 | -0.43426 |
| C | 0.65693 | -1.75070 | -0.77727 |
| O | 1.35602 | -2.22266 | -1.64423 |
| C | -0.27065 | -2.55758 | 0.09911 |
| H | -0.41781 | -3.53123 | -0.37531 |
| H | 0.28209 | -2.72815 | 1.03106 |
| C | -1.59603 | -1.89987 | 0.51049 |
| H | -1.39880 | -0.83757 | 0.69954 |
| O | -1.99417 | -2.52962 | 1.71730 |
| H | -2.29225 | -1.81579 | 2.30951 |
| C | -2.70152 | -2.00207 | -0.58422 |
| C | -2.13055 | -1.64076 | -1.95628 |
| H | -2.92711 | -1.61556 | -2.70396 |
| H | -1.38969 | -2.38030 | -2.27599 |
| H | -1.65785 | -0.65158 | -1.93999 |
| C | -3.29437 | -3.42162 | -0.62447 |
| H | -2.51310 | -4.14953 | -0.86945 |
| H | -4.06592 | -3.48762 | -1.39944 |
| H | -3.73111 | -3.70830 | 0.33485 |
| C | -3.87432 | -1.05080 | -0.28485 |
| O | -4.31771 | -0.32180 | -1.15363 |
| C | -4.58563 | -1.07507 | 1.07207 |
| H | -4.29331 | -1.97490 | 1.61840 |
| C | -6.09739 | -1.11688 | 0.82679 |
| H | -6.36151 | -1.97877 | 0.20601 |
| H | -6.43791 | -0.21623 | 0.30912 |
| H | -6.63366 | -1.20364 | 1.77662 |
| C | -4.23266 | 0.12029 | 1.98646 |
| H | -5.00040 | 0.11192 | 2.77499 |
| O | -2.97082 | -0.16324 | 2.59591 |
| H | -2.74423 | 0.55484 | 3.20947 |
| C | -4.24091 | 1.51568 | 1.32899 |
| H | -5.01743 | 1.50287 | 0.55326 |
| C | -4.62278 | 2.57051 | 2.37295 |
| H | -5.60478 | 2.35613 | 2.80751 |
| H | -3.89183 | 2.59755 | 3.19254 |
| H | -4.66433 | 3.57349 | 1.93914 |
| C | -2.90583 | 1.86743 | 0.65191 |
| H | -2.54266 | 1.02195 | 0.05559 |
| H | -2.13985 | 2.04648 | 1.41992 |
| C | -3.00349 | 3.09463 | -0.25451 |
| H | -3.22296 | 3.98719 | 0.34238 |
| H | -3.84712 | 2.96974 | -0.94624 |
| C | -1.71662 | 3.35444 | -1.05067 |
| H | -0.88300 | 3.49666 | -0.35464 |
| H | -1.83429 | 4.30458 | -1.59156 |
| C | -1.39403 | 2.28647 | -2.07030 |
| C | -0.21927 | 1.65011 | -2.15706 |
| C | 0.97839 | 1.76401 | -1.25281 |
| C | 2.90071 | 0.42820 | -0.24653 |
| C | 4.03132 | -0.04393 | -0.79534 |
| H | 3.97030 | -0.46108 | -1.79929 |
| C | 2.74750 | 0.99728 | 1.13928 |
| H | 3.44476 | 0.54362 | 1.84330 |
| H | 1.72510 | 0.83750 | 1.49643 |
| H | 2.93689 | 2.07818 | 1.14552 |
| C | 5.37967 | -0.07999 | -0.22646 |
| C | 6.41674 | -0.73709 | -0.83000 |
| C | 6.97000 | 0.40296 | 1.24986 |
| H | 6.39701 | -1.30424 | -1.75115 |
| C | 7.63547 | 0.97037 | 2.46222 |
| H | 8.48353 | 1.60527 | 2.18928 |
| H | 8.00613 | 0.17434 | 3.11536 |
| H | 6.90719 | 1.56831 | 3.01346 |
| S | 7.85702 | -0.56187 | 0.09084 |
| N | 5.71900 | 0.56607 | 0.95278 |
| C | -2.49816 | 1.96819 | -3.04719 |
| H | -3.30119 | 1.40486 | -2.55515 |
| H | -2.12861 | 1.36082 | -3.87900 |
| H | 0.70745 | 2.16329 | -0.27012 |
| H | -0.09521 | 0.94017 | -2.97852 |
| H | 1.73325 | 2.43811 | -1.68118 |
| H | -2.94310 | 2.88400 | -3.45654 |

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Compound **5.33**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -21.597918 kJ.

| | | | |
|---|---|---|---|
| C | -1.77130 | 2.60010 | -0.35170 |
| O | -1.82730 | 3.08430 | -1.48060 |
| C | -3.07960 | 2.19700 | 0.34340 |
| H | -3.87550 | 2.37390 | -0.37990 |
| C | -3.10710 | 0.69760 | 0.73520 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.30620 | 0.50780 | 1.44810 | H | 6.41980 | 1.74670 | -0.30870 |
| H | -4.01730 | 0.49410 | 1.29890 | H | 5.26390 | 3.04600 | -0.50840 |
| C | -3.36540 | 3.10860 | 1.54970 | C | 2.96500 | 1.64570 | -0.44910 |
| H | -4.37310 | 2.94150 | 1.93050 | H | 2.79530 | 1.59830 | -1.51640 |
| H | -3.29310 | 4.16230 | 1.27580 | C | 1.94630 | 2.01840 | 0.35250 |
| H | -2.67010 | 2.92800 | 2.36990 | C | 2.11430 | 2.08390 | 1.86480 |
| C | -2.99520 | -0.31430 | -0.44090 | H | 1.32160 | 2.65130 | 2.34950 |
| H | -2.11350 | -0.04690 | -1.01760 | H | 3.04510 | 2.58540 | 2.12970 |
| C | -4.13740 | -0.18290 | -1.48670 | H | 2.12880 | 1.07870 | 2.28740 |
| H | -4.00540 | -0.93440 | -2.26630 | C | 0.67420 | 2.32710 | -0.28260 |
| H | -4.00300 | 0.76880 | -2.00260 | H | 0.67240 | 2.52470 | -1.34720 |
| C | -5.59350 | -0.22610 | -0.98270 | C | -0.50750 | 2.35830 | 0.36190 |
| H | -5.76300 | 0.48100 | -0.17030 | H | -0.57490 | 2.13850 | 1.41500 |
| H | -6.25870 | 0.07390 | -1.79400 | | | | |
| O | -5.95910 | -1.53180 | -0.58270 | --- | | | |
| H | -6.89480 | -1.55290 | -0.42700 | | | | |
| C | -2.75850 | -1.78110 | 0.02600 | Compound **5.33** | | | |
| H | -2.85260 | -2.44040 | -0.83900 | This structure was assigned as ambiguous. | | | |
| O | -3.79780 | -2.10800 | 0.91910 | | | | |
| H | -4.61860 | -1.98850 | 0.43200 | Molecular Mechanics (OPLS-2005), gas | | | |
| C | -1.39280 | -2.09480 | 0.71260 | phase. | | | |
| H | -1.31100 | -1.48820 | 1.61440 | Energy: -15.805611 kJ. | | | |
| C | -1.34060 | -3.57280 | 1.15940 | | | | |
| H | -0.43640 | -3.79840 | 1.72260 | C | -1.60070 | 2.68930 | 0.62120 |
| H | -1.38320 | -4.24680 | 0.30380 | O | -2.14800 | 3.61730 | 0.02790 |
| H | -2.17470 | -3.82440 | 1.81490 | C | -2.44190 | 1.82910 | 1.57690 |
| C | -0.18040 | -1.76740 | -0.19490 | H | -3.47430 | 2.14770 | 1.42910 |
| H | -0.18940 | -0.70940 | -0.45210 | C | -2.38050 | 0.30300 | 1.29320 |
| H | -0.27480 | -2.30930 | -1.13730 | H | -1.41030 | -0.06890 | 1.61920 |
| C | 1.20100 | -2.06120 | 0.42920 | H | -3.10320 | -0.18440 | 1.94940 |
| H | 1.34400 | -3.13250 | 0.56440 | C | -2.08840 | 2.14510 | 3.04030 |
| H | 1.27010 | -1.59900 | 1.41390 | H | -2.79110 | 1.66430 | 3.72130 |
| C | 2.34950 | -1.54170 | -0.43580 | H | -2.13140 | 3.21790 | 3.23490 |
| O | 2.28840 | -1.55190 | -1.66550 | H | -1.08700 | 1.79940 | 3.29880 |
| O | 3.37010 | -1.05650 | 0.29840 | C | -2.65720 | -0.17400 | -0.16210 |
| C | 4.46140 | -0.37940 | -0.32620 | H | -1.84410 | 0.18480 | -0.79350 |
| H | 4.44120 | -0.51680 | -1.40870 | C | -3.96620 | 0.46640 | -0.71310 |
| C | 5.75860 | -1.01590 | 0.21220 | H | -3.82810 | 1.54590 | -0.76010 |
| H | 5.80880 | -0.89550 | 1.29500 | H | -4.78690 | 0.31760 | -0.00920 |
| H | 6.62330 | -0.49370 | -0.19520 | C | -4.40860 | 0.03010 | -2.12020 |
| C | 5.89590 | -2.50230 | -0.14830 | H | -5.08980 | 0.77510 | -2.53480 |
| H | 5.09980 | -3.09650 | 0.30100 | H | -3.55810 | -0.03740 | -2.80050 |
| H | 6.84570 | -2.90300 | 0.20600 | O | -5.09870 | -1.20370 | -2.05320 |
| H | 5.85300 | -2.65020 | -1.22790 | H | -5.45650 | -1.40190 | -2.90860 |
| C | 4.33530 | 1.13700 | -0.01630 | C | -2.65550 | -1.73000 | -0.27700 |
| H | 4.44770 | 1.25910 | 1.05950 | H | -2.69290 | -1.99730 | -1.33410 |
| C | 5.42750 | 1.98330 | -0.69110 | O | -3.85440 | -2.18670 | 0.30780 |
| H | 5.43860 | 1.83090 | -1.77090 | H | -4.54780 | -1.92490 | -0.29700 |

| | | | |
|---|---|---|---|
| C | -1.45990 | -2.51230 | 0.34110 |
| H | -1.45280 | -2.33450 | 1.41710 |
| C | -1.65450 | -4.03260 | 0.14310 |
| H | -0.89280 | -4.61460 | 0.65940 |
| H | -1.62890 | -4.30270 | -0.91260 |
| H | -2.61060 | -4.37090 | 0.54310 |
| C | -0.09480 | -2.06230 | -0.23490 |
| H | 0.03160 | -0.99430 | -0.06240 |
| H | -0.09300 | -2.19490 | -1.31780 |
| C | 1.11800 | -2.80520 | 0.36910 |
| H | 1.08650 | -3.86400 | 0.11470 |
| H | 1.09720 | -2.73840 | 1.45680 |
| C | 2.45510 | -2.25390 | -0.11790 |
| O | 3.19170 | -2.90730 | -0.85390 |
| O | 2.69200 | -1.01740 | 0.34140 |
| C | 3.87430 | -0.30240 | -0.01470 |
| H | 4.66250 | -0.98800 | -0.33110 |
| C | 4.37050 | 0.41250 | 1.25630 |
| H | 3.59320 | 1.07560 | 1.63800 |
| H | 5.21810 | 1.05010 | 1.00300 |
| C | 4.80690 | -0.55860 | 2.36220 |
| H | 3.97470 | -1.17770 | 2.69850 |
| H | 5.18650 | -0.01690 | 3.22860 |
| H | 5.59710 | -1.22370 | 2.01240 |
| C | 3.57790 | 0.69210 | -1.16840 |
| H | 4.36790 | 1.44270 | -1.17950 |
| C | 3.61520 | 0.00890 | -2.54390 |
| H | 2.83430 | -0.74540 | -2.64260 |
| H | 4.57230 | -0.48650 | -2.71010 |
| H | 3.47670 | 0.73430 | -3.34600 |
| C | 2.23500 | 1.37340 | -0.96120 |
| H | 1.39120 | 0.70660 | -1.06590 |
| C | 1.99460 | 2.65850 | -0.63720 |
| C | 3.11080 | 3.66700 | -0.45440 |
| H | 3.67570 | 3.78460 | -1.37960 |
| H | 3.79360 | 3.34830 | 0.33330 |
| H | 2.71150 | 4.64350 | -0.17810 |
| C | 0.62110 | 3.04850 | -0.38710 |
| H | 0.21580 | 3.88690 | -0.93830 |
| C | -0.17980 | 2.35820 | 0.44810 |
| H | 0.20630 | 1.51160 | 0.99580 |

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Compound **5.33**
This structure was assigned as ambiguous.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1274.90594171 hartree.
Free Energy: -1274.376785 hartree.

| | | | |
|---|---|---|---|
| C | -1.57731 | 2.72780 | 0.28310 |
| O | -1.96949 | 3.74144 | -0.27398 |
| C | -2.50713 | 1.93961 | 1.19443 |
| H | -3.51930 | 2.25905 | 0.92171 |
| C | -2.39743 | 0.41001 | 1.09025 |
| H | -1.47312 | 0.08371 | 1.58647 |
| H | -3.21925 | -0.01463 | 1.67890 |
| C | -2.22751 | 2.39133 | 2.63629 |
| H | -2.90006 | 1.87545 | 3.32943 |
| H | -2.37860 | 3.46930 | 2.74790 |
| H | -1.19709 | 2.15588 | 2.92703 |
| C | -2.43182 | -0.18342 | -0.32937 |
| H | -1.46317 | 0.02064 | -0.80651 |
| C | -3.47204 | 0.48558 | -1.25373 |
| H | -3.40563 | 0.03140 | -2.25108 |
| H | -3.17562 | 1.53427 | -1.37945 |
| C | -4.94627 | 0.46034 | -0.84041 |
| H | -5.05040 | 0.67319 | 0.23565 |
| H | -5.47089 | 1.25974 | -1.37449 |
| O | -5.60919 | -0.74057 | -1.18157 |
| H | -5.16270 | -1.42242 | -0.64710 |
| C | -2.55793 | -1.71531 | -0.28083 |
| H | -2.60898 | -2.08054 | -1.32048 |
| O | -3.79515 | -2.01194 | 0.38186 |
| H | -3.91756 | -2.97445 | 0.39054 |
| C | -1.41073 | -2.46801 | 0.42813 |
| H | -1.46184 | -2.21514 | 1.49658 |
| C | -1.61219 | -3.98155 | 0.28381 |
| H | -0.88355 | -4.53845 | 0.87823 |
| H | -1.50231 | -4.28908 | -0.76356 |
| H | -2.59533 | -4.31526 | 0.63254 |
| C | -0.03249 | -2.04454 | -0.10333 |
| H | 0.15339 | -0.99674 | 0.15634 |
| H | -0.02735 | -2.11106 | -1.20138 |
| C | 1.11925 | -2.89202 | 0.45789 |
| H | 1.05745 | -3.92915 | 0.12516 |
| H | 1.08029 | -2.88128 | 1.55530 |
| C | 2.48000 | -2.38538 | 0.03882 |
| O | 3.32210 | -3.04714 | -0.52320 |
| O | 2.64001 | -1.09829 | 0.38182 |
| C | 3.85838 | -0.40958 | 0.02041 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 4.62554 | -1.16078 | -0.19314 | H | -2.02883 | -0.02192 | -0.97322 |
| C | 4.26175 | 0.42311 | 1.22814 | C | -4.05329 | -0.14071 | -1.51079 |
| H | 3.46322 | 1.14268 | 1.44647 | H | -3.88879 | -0.88917 | -2.29765 |
| H | 5.15141 | 1.00143 | 0.95171 | H | -3.92075 | 0.83547 | -1.99322 |
| C | 4.55298 | -0.43613 | 2.45430 | C | -5.51672 | -0.22824 | -1.08935 |
| H | 3.66634 | -1.00449 | 2.75183 | H | -5.72585 | 0.43660 | -0.23919 |
| H | 4.85740 | 0.18181 | 3.30413 | H | -6.14771 | 0.09716 | -1.92853 |
| H | 5.35893 | -1.14982 | 2.24993 | O | -5.84687 | -1.58775 | -0.75274 |
| C | 3.58571 | 0.42827 | -1.24604 | H | -6.76726 | -1.61267 | -0.44891 |
| H | 4.43274 | 1.11582 | -1.34920 | C | -2.75479 | -1.76286 | 0.04619 |
| C | 3.50828 | -0.45373 | -2.49614 | H | -2.81101 | -2.40358 | -0.85341 |
| H | 2.65976 | -1.14484 | -2.43845 | O | -3.77085 | -2.13926 | 0.96983 |
| H | 4.41959 | -1.04814 | -2.61527 | H | -4.61505 | -2.10944 | 0.47506 |
| H | 3.37561 | 0.16151 | -3.39164 | C | -1.39719 | -2.08075 | 0.72787 |
| C | 2.30043 | 1.18563 | -1.06578 | H | -1.35075 | -1.49572 | 1.65843 |
| H | 1.40871 | 0.56358 | -1.15001 | C | -1.35913 | -3.56980 | 1.11319 |
| C | 2.10964 | 2.48675 | -0.79405 | H | -0.48784 | -3.80485 | 1.73448 |
| C | 3.18725 | 3.53477 | -0.69663 | H | -1.31090 | -4.20239 | 0.21610 |
| H | 4.16629 | 3.15943 | -1.00138 | H | -2.25920 | -3.83846 | 1.66916 |
| H | 3.26993 | 3.91016 | 0.33009 | C | -0.19821 | -1.68658 | -0.15742 |
| H | 2.93792 | 4.39455 | -1.32959 | H | -0.23031 | -0.61422 | -0.37267 |
| C | 0.73085 | 2.95164 | -0.56127 | H | -0.26459 | -2.19488 | -1.12773 |
| H | 0.43687 | 3.91854 | -0.97303 | C | 1.17913 | -1.98578 | 0.45862 |
| C | -0.17548 | 2.25891 | 0.14681 | H | 1.34212 | -3.06772 | 0.54824 |
| H | 0.10796 | 1.33186 | 0.64148 | H | 1.26829 | -1.57132 | 1.46857 |
| ---------- | | | | C | 2.29668 | -1.43124 | -0.40496 |
| | | | | O | 2.27520 | -1.38930 | -1.61652 |
| Compound **5.33** | | | | O | 3.33436 | -0.98862 | 0.35341 |
| This structure was assigned as correct. | | | | C | 4.45006 | -0.35267 | -0.32642 |
| B3LYP/6-31g(d) | | | | H | 4.34849 | -0.56002 | -1.39607 |
| Gas phase. | | | | C | 5.72800 | -0.98911 | 0.22511 |
| | | | | H | 5.78264 | -0.79176 | 1.30428 |
| Electronic Energy: -1275.43978235 hartree. | | | | H | 6.59052 | -0.48995 | -0.23137 |
| | | | | C | 5.81883 | -2.49626 | -0.03607 |
| Free Energy: -1274.916193 hartree. | | | | H | 4.99460 | -3.03001 | 0.44678 |
| | | | | H | 6.75830 | -2.90135 | 0.35553 |
| C | -1.79036 | 2.53203 | -0.34952 | H | 5.78026 | -2.71645 | -1.10950 |
| O | -1.81896 | 2.82849 | -1.53965 | C | 4.35337 | 1.18209 | -0.08444 |
| C | -3.08231 | 2.18542 | 0.39835 | H | 4.53870 | 1.34909 | 0.98282 |
| H | -3.88730 | 2.40693 | -0.31122 | C | 5.42097 | 1.94706 | -0.89285 |
| C | -3.10288 | 0.67734 | 0.75522 | H | 5.31463 | 1.75348 | -1.96731 |
| H | -2.30157 | 0.48322 | 1.47927 | H | 6.43671 | 1.66801 | -0.59679 |
| H | -4.03117 | 0.45334 | 1.29355 | H | 5.31350 | 3.02542 | -0.73689 |
| C | -3.29836 | 3.05291 | 1.65172 | C | 2.97940 | 1.67566 | -0.45208 |
| H | -4.28025 | 2.84044 | 2.09046 | H | 2.78123 | 1.69808 | -1.52452 |
| H | -3.26241 | 4.12160 | 1.41172 | C | 1.95773 | 2.00889 | 0.37049 |
| H | -2.54793 | 2.85442 | 2.42555 | C | 2.04048 | 2.01370 | 1.87909 |
| C | -2.94356 | -0.29448 | -0.43445 | H | 1.65095 | 2.95541 | 2.28387 |

| | | | |
|---|---|---|---|
| H | 3.06107 | 1.88708 | 2.24352 |
| H | 1.43574 | 1.20489 | 2.30848 |
| C | 0.66690 | 2.30499 | -0.24487 |
| H | 0.64431 | 2.38615 | -1.33105 |
| C | -0.51689 | 2.40199 | 0.39920 |
| H | -0.57272 | 2.28896 | 1.47768 |

---

Compound **5.33**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1274.91640766 hartree.
Free Energy: -1274.386582 hartree.

| | | | |
|---|---|---|---|
| C | -1.87213 | 2.49103 | -0.30631 |
| O | -1.88223 | 2.91828 | -1.45046 |
| C | -3.15916 | 2.10558 | 0.40818 |
| H | -3.96805 | 2.30621 | -0.30356 |
| C | -3.13077 | 0.60690 | 0.75696 |
| H | -2.35119 | 0.43622 | 1.51068 |
| H | -4.07483 | 0.33983 | 1.24596 |
| C | -3.37965 | 2.95958 | 1.66094 |
| H | -4.34376 | 2.70925 | 2.11573 |
| H | -3.38493 | 4.02773 | 1.42155 |
| H | -2.60264 | 2.78133 | 2.41220 |
| C | -2.88543 | -0.31883 | -0.44195 |
| H | -1.95223 | -0.00919 | -0.92894 |
| C | -3.95330 | -0.16031 | -1.54734 |
| H | -3.78485 | -0.92255 | -2.31916 |
| H | -3.79767 | 0.81007 | -2.03490 |
| C | -5.41558 | -0.21463 | -1.14110 |
| H | -5.62980 | 0.50348 | -0.33814 |
| H | -6.03658 | 0.05740 | -2.00372 |
| O | -5.74309 | -1.54151 | -0.72336 |
| H | -6.66466 | -1.54891 | -0.41844 |
| C | -2.67263 | -1.77910 | 0.01777 |
| H | -2.69738 | -2.41384 | -0.88808 |
| O | -3.67884 | -2.19263 | 0.92528 |
| H | -4.53198 | -2.08155 | 0.45904 |
| C | -1.32140 | -2.05379 | 0.70889 |
| H | -1.31659 | -1.50647 | 1.66308 |
| C | -1.21305 | -3.54944 | 1.01696 |
| H | -0.35082 | -3.77064 | 1.65376 |
| H | -1.10119 | -4.12372 | 0.08759 |
| H | -2.11303 | -3.89879 | 1.52743 |
| C | -0.14141 | -1.56911 | -0.14147 |
| H | -0.16420 | -0.47699 | -0.22189 |
| H | -0.23871 | -1.95991 | -1.16307 |
| C | 1.23494 | -1.96035 | 0.40192 |
| H | 1.38705 | -3.04553 | 0.34868 |
| H | 1.35745 | -1.66820 | 1.44954 |
| C | 2.32230 | -1.32072 | -0.42916 |
| O | 2.26096 | -1.17994 | -1.62967 |
| O | 3.37155 | -0.94007 | 0.31931 |
| C | 4.44784 | -0.23436 | -0.33298 |
| H | 4.34043 | -0.37008 | -1.41382 |
| C | 5.74734 | -0.86575 | 0.14753 |
| H | 5.84631 | -0.69891 | 1.22778 |
| H | 6.58194 | -0.34994 | -0.33807 |
| C | 5.81297 | -2.35733 | -0.16892 |
| H | 5.01288 | -2.90250 | 0.34037 |
| H | 6.76886 | -2.78226 | 0.15114 |
| H | 5.70927 | -2.53260 | -1.24569 |
| C | 4.30490 | 1.26295 | 0.01262 |
| H | 4.44342 | 1.35903 | 1.09538 |
| C | 5.37528 | 2.09526 | -0.70065 |
| H | 5.33975 | 1.92699 | -1.78343 |
| H | 6.37995 | 1.84764 | -0.34794 |
| H | 5.20988 | 3.16147 | -0.51934 |
| C | 2.93169 | 1.73638 | -0.37558 |
| H | 2.81100 | 1.99126 | -1.43061 |
| C | 1.84419 | 1.82024 | 0.41541 |
| C | 1.82100 | 1.46436 | 1.87840 |
| H | 1.50105 | 2.32139 | 2.48256 |
| H | 2.79166 | 1.12752 | 2.24186 |
| H | 1.09978 | 0.65780 | 2.05987 |
| C | 0.57628 | 2.21669 | -0.19956 |
| H | 0.59353 | 2.44912 | -1.26475 |
| C | -0.60949 | 2.24734 | 0.43456 |
| H | -0.68415 | 2.00014 | 1.48986 |

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Compound **5.33**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1275.47189643 hartree.
Free Energy: -1274.948736 hartree.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.78005 | 2.56060 | -0.38766 | H | 5.68770 | -2.66707 | -1.26339 |
| O | -1.78279 | 2.90319 | -1.57027 | C | 4.34848 | 1.20261 | -0.02046 |
| C | -3.08760 | 2.19437 | 0.31911 | H | 4.51415 | 1.31681 | 1.05629 |
| H | -3.87563 | 2.38417 | -0.41761 | C | 5.44133 | 1.98700 | -0.77321 |
| C | -3.10053 | 0.69641 | 0.71618 | H | 5.36751 | 1.82956 | -1.85652 |
| H | -2.30597 | 0.52951 | 1.45398 | H | 6.44590 | 1.69291 | -0.45392 |
| H | -4.03777 | 0.48918 | 1.24518 | H | 5.33454 | 3.06061 | -0.58327 |
| C | -3.35354 | 3.09189 | 1.54198 | C | 2.98775 | 1.72471 | -0.39841 |
| H | -4.34595 | 2.87509 | 1.95483 | H | 2.81391 | 1.78671 | -1.47424 |
| H | -3.32871 | 4.15433 | 1.27195 | C | 1.95157 | 2.04623 | 0.41312 |
| H | -2.62180 | 2.92835 | 2.34151 | C | 2.00133 | 2.01311 | 1.92188 |
| C | -2.92639 | -0.30726 | -0.44561 | H | 1.61736 | 2.95072 | 2.34224 |
| H | -2.00535 | -0.04706 | -0.98049 | H | 3.01329 | 1.86495 | 2.30339 |
| C | -4.03069 | -0.19010 | -1.53371 | H | 1.37456 | 1.20525 | 2.32089 |
| H | -3.85704 | -0.96111 | -2.29710 | C | 0.67624 | 2.35495 | -0.22678 |
| H | -3.90360 | 0.77155 | -2.04576 | H | 0.68938 | 2.46346 | -1.31099 |
| C | -5.49603 | -0.26518 | -1.11785 | C | -0.52704 | 2.42299 | 0.38785 |
| H | -5.71815 | 0.43549 | -0.30216 | H | -0.61145 | 2.27756 | 1.46044 |
| H | -6.12389 | 0.01585 | -1.97455 | ---------- | | | |
| O | -5.82504 | -1.61085 | -0.71929 | | | | |
| H | -6.74039 | -1.61013 | -0.38963 | Compound **5.33** | | | |
| C | -2.73914 | -1.76509 | 0.07059 | This structure was assigned as ambiguous. | | | |
| H | -2.79722 | -2.42625 | -0.81356 | B3LYP/6-31g(d) | | | |
| O | -3.76475 | -2.12011 | 0.99827 | Gas phase. | | | |
| H | -4.61072 | -2.05086 | 0.50380 | | | | |
| C | -1.38253 | -2.07148 | 0.75957 | Electronic Energy: -1275.43211775 har- | | | |
| H | -1.30230 | -1.42533 | 1.64616 | tree. | | | |
| C | -1.36506 | -3.53093 | 1.24471 | Free Energy: -1274.908856 hartree. | | | |
| H | -0.46834 | -3.74783 | 1.83580 | | | | |
| H | -1.38027 | -4.22767 | 0.39480 | C | -1.38245 | 2.87982 | 0.47752 |
| H | -2.23882 | -3.74082 | 1.86585 | O | -1.82777 | 3.83358 | -0.15289 |
| C | -0.18502 | -1.77004 | -0.16465 | C | -2.25925 | 2.14322 | 1.49676 |
| H | -0.21217 | -0.72083 | -0.47412 | H | -3.26600 | 2.54547 | 1.34506 |
| H | -0.26554 | -2.36420 | -1.08409 | C | -2.28779 | 0.60360 | 1.33469 |
| C | 1.19068 | -2.02755 | 0.47728 | H | -1.32960 | 0.19675 | 1.68252 |
| H | 1.36406 | -3.10281 | 0.61418 | H | -3.04722 | 0.21415 | 2.02491 |
| H | 1.26038 | -1.56579 | 1.46740 | C | -1.81028 | 2.52087 | 2.92400 |
| C | 2.31366 | -1.50327 | -0.39589 | H | -2.46546 | 2.04710 | 3.66412 |
| O | 2.32583 | -1.57004 | -1.61064 | H | -1.85121 | 3.60464 | 3.07704 |
| O | 3.30429 | -0.95847 | 0.34546 | H | -0.78508 | 2.18758 | 3.12522 |
| C | 4.42405 | -0.31769 | -0.33658 | C | -2.59830 | 0.04414 | -0.07252 |
| H | 4.29282 | -0.47608 | -1.41035 | H | -1.74729 | 0.25622 | -0.73731 |
| C | 5.70253 | -1.00226 | 0.15011 | C | -3.83290 | 0.76413 | -0.67571 |
| H | 5.79298 | -0.85430 | 1.23469 | H | -3.57299 | 1.81436 | -0.84638 |
| H | 6.56008 | -0.49980 | -0.31105 | H | -4.65562 | 0.76312 | 0.05094 |
| C | 5.75666 | -2.49660 | -0.18197 | C | -4.38425 | 0.21481 | -1.98890 |
| H | 4.93865 | -3.04431 | 0.29853 | H | -4.99341 | 0.98561 | -2.48208 |
| H | 6.69971 | -2.93423 | 0.16522 | H | -3.56672 | -0.05517 | -2.67503 |

| | | | |
|---|---|---|---|
| O | -5.20636 | -0.93102 | -1.70769 |
| H | -5.43462 | -1.36747 | -2.54182 |
| C | -2.79278 | -1.50117 | -0.04171 |
| H | -2.87346 | -1.83819 | -1.08845 |
| O | -3.99937 | -1.82288 | 0.64706 |
| H | -4.71183 | -1.66784 | -0.00112 |
| C | -1.65993 | -2.34146 | 0.59983 |
| H | -1.60545 | -2.06975 | 1.66362 |
| C | -2.02675 | -3.83321 | 0.51793 |
| H | -1.33829 | -4.45339 | 1.10110 |
| H | -1.99605 | -4.18689 | -0.52201 |
| H | -3.03677 | -3.99011 | 0.90075 |
| C | -0.28808 | -2.05159 | -0.04531 |
| H | -0.04288 | -0.99105 | 0.06677 |
| H | -0.34521 | -2.25159 | -1.12555 |
| C | 0.87177 | -2.87923 | 0.55367 |
| H | 0.73842 | -3.94491 | 0.35875 |
| H | 0.89793 | -2.72850 | 1.64068 |
| C | 2.22692 | -2.49778 | -0.01493 |
| O | 2.91489 | -3.20447 | -0.71915 |
| O | 2.56716 | -1.24137 | 0.36979 |
| C | 3.83169 | -0.67008 | -0.07222 |
| H | 4.46478 | -1.49495 | -0.41336 |
| C | 4.45552 | 0.01395 | 1.14552 |
| H | 3.79289 | 0.82333 | 1.47712 |
| H | 5.38934 | 0.48806 | 0.81497 |
| C | 4.74719 | -0.93978 | 2.30762 |
| H | 3.82714 | -1.40183 | 2.67891 |
| H | 5.21457 | -0.40459 | 3.14131 |
| H | 5.42805 | -1.74351 | 2.00229 |
| C | 3.58025 | 0.30686 | -1.25883 |
| H | 4.47422 | 0.93917 | -1.32284 |
| C | 3.43132 | -0.44469 | -2.59774 |
| H | 2.55514 | -1.10090 | -2.59341 |
| H | 4.30889 | -1.06963 | -2.79615 |
| H | 3.31758 | 0.26579 | -3.42343 |
| C | 2.35904 | 1.14343 | -0.99016 |
| H | 1.45042 | 0.55416 | -0.90470 |
| C | 2.21668 | 2.47870 | -0.86056 |
| C | 3.31092 | 3.50376 | -1.04927 |
| H | 4.25275 | 3.05752 | -1.37803 |
| H | 3.50336 | 4.05395 | -0.11927 |
| H | 3.01189 | 4.24857 | -1.79850 |
| C | 0.87492 | 2.99937 | -0.55054 |
| H | 0.55351 | 3.92231 | -1.03557 |
| C | 0.01091 | 2.40666 | 0.29869 |
| H | 0.32965 | 1.53564 | 0.86499 |

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Compound **5.33**
This structure was assigned as ambiguous.
B3LYP/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1275.46282788 hartree.
Free Energy: -1274.941120 hartree.

| | | | |
|---|---|---|---|
| C | -1.39113 | 2.90664 | 0.47712 |
| O | -1.81649 | 3.89897 | -0.11449 |
| C | -2.28754 | 2.15421 | 1.46508 |
| H | -3.29520 | 2.54526 | 1.29156 |
| C | -2.29736 | 0.61321 | 1.31186 |
| H | -1.33646 | 0.22036 | 1.66594 |
| H | -3.05523 | 0.22886 | 2.00690 |
| C | -1.87636 | 2.54030 | 2.90199 |
| H | -2.55134 | 2.06800 | 3.62563 |
| H | -1.92606 | 3.62507 | 3.05093 |
| H | -0.85565 | 2.21218 | 3.13254 |
| C | -2.60113 | 0.03475 | -0.08928 |
| H | -1.75001 | 0.24285 | -0.75372 |
| C | -3.83930 | 0.73783 | -0.70809 |
| H | -3.57313 | 1.77887 | -0.92150 |
| H | -4.65463 | 0.77535 | 0.02670 |
| C | -4.41018 | 0.14600 | -1.99453 |
| H | -5.00911 | 0.90649 | -2.51494 |
| H | -3.60797 | -0.16902 | -2.67661 |
| O | -5.25852 | -0.97159 | -1.66474 |
| H | -5.41602 | -1.48899 | -2.47213 |
| C | -2.78104 | -1.51175 | -0.04531 |
| H | -2.85097 | -1.85640 | -1.08965 |
| O | -3.99906 | -1.83899 | 0.63120 |
| H | -4.69739 | -1.66886 | -0.03304 |
| C | -1.64712 | -2.34030 | 0.61014 |
| H | -1.59300 | -2.05930 | 1.67160 |
| C | -2.00249 | -3.83521 | 0.53991 |
| H | -1.31400 | -4.44507 | 1.13431 |
| H | -1.96347 | -4.20038 | -0.49595 |
| H | -3.01391 | -4.00205 | 0.91790 |
| C | -0.27497 | -2.04992 | -0.03532 |
| H | -0.03362 | -0.98859 | 0.07530 |
| H | -0.33082 | -2.25332 | -1.11464 |
| C | 0.88490 | -2.87512 | 0.56793 |
| H | 0.74781 | -3.94238 | 0.38303 |
| H | 0.91727 | -2.71676 | 1.65375 |

| | | | |
|---|---|---|---|
| C | 2.23923 | -2.50138 | -0.00479 |
| O | 2.93446 | -3.23071 | -0.68576 |
| O | 2.57611 | -1.24188 | 0.34717 |
| C | 3.84266 | -0.66319 | -0.09268 |
| H | 4.47412 | -1.48028 | -0.45273 |
| C | 4.47635 | -0.00744 | 1.13457 |
| H | 3.80830 | 0.77994 | 1.50643 |
| H | 5.39617 | 0.48995 | 0.80121 |
| C | 4.80479 | -0.99327 | 2.25855 |
| H | 3.90183 | -1.48722 | 2.63388 |
| H | 5.27682 | -0.47595 | 3.10175 |
| H | 5.49716 | -1.77242 | 1.91573 |
| C | 3.57940 | 0.33246 | -1.25944 |
| H | 4.47163 | 0.96550 | -1.32164 |
| C | 3.41742 | -0.40084 | -2.60599 |
| H | 2.53857 | -1.05535 | -2.60531 |
| H | 4.29689 | -1.01818 | -2.82290 |
| H | 3.29672 | 0.31994 | -3.42243 |
| C | 2.35808 | 1.16370 | -0.97321 |
| H | 1.44923 | 0.57353 | -0.89056 |
| C | 2.21921 | 2.50001 | -0.83596 |
| C | 3.31549 | 3.52344 | -1.01651 |
| H | 4.25917 | 3.07569 | -1.33828 |
| H | 3.50143 | 4.07250 | -0.08402 |
| H | 3.02150 | 4.26992 | -1.76637 |
| C | 0.87954 | 3.02524 | -0.52656 |
| H | 0.58843 | 3.97051 | -0.98696 |
| C | -0.00717 | 2.41892 | 0.29199 |
| H | 0.28530 | 1.52343 | 0.83252 |

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Compound **5.34**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -44.726128 kJ.

| | | | |
|---|---|---|---|
| O | -6.23400 | 5.56130 | 7.11160 |
| C | -6.66570 | 6.73720 | 6.62250 |
| O | -7.83550 | 7.02490 | 6.37590 |
| C | -7.13040 | 4.46080 | 7.20960 |
| H | -6.55160 | 3.53870 | 7.25620 |
| H | -7.68940 | 4.39990 | 6.27520 |
| C | -8.10470 | 4.53370 | 8.41270 |
| O | -9.31110 | 3.88410 | 8.02430 |
| H | -8.32900 | 5.57060 | 8.67110 |
| C | -7.56630 | 3.82170 | 9.67920 |
| C | -10.22430 | 4.71990 | 7.32580 |
| H | -11.11760 | 4.14900 | 7.07290 |
| H | -10.53470 | 5.56570 | 7.94070 |
| H | -9.80250 | 5.10310 | 6.39680 |
| C | -8.67790 | 3.61430 | 10.73150 |
| C | -6.35070 | 4.55180 | 10.24460 |
| H | -7.22080 | 2.82970 | 9.38560 |
| H | -9.10520 | 4.56420 | 11.05430 |
| H | -8.30420 | 3.08870 | 11.61050 |
| H | -9.49360 | 3.00980 | 10.33390 |
| C | -6.21350 | 5.03240 | 11.49480 |
| H | -5.53530 | 4.69910 | 9.55050 |
| H | -7.01070 | 4.93340 | 12.21630 |
| C | -5.01220 | 5.81370 | 11.98690 |
| C | -5.37910 | 7.28980 | 12.09330 |
| H | -4.17640 | 5.70380 | 11.29610 |
| H | -4.69400 | 5.43720 | 12.95900 |
| O | -5.46920 | 7.85260 | 13.18320 |
| O | -5.61380 | 7.84140 | 10.89570 |
| C | -5.95890 | 9.21440 | 10.79230 |
| C | -4.71660 | 10.09640 | 10.51250 |
| H | -6.65250 | 9.30430 | 9.95640 |
| H | -6.51230 | 9.55780 | 11.66630 |
| H | -5.06580 | 11.09630 | 10.24860 |
| C | -3.83120 | 9.57750 | 9.35530 |
| O | -3.88070 | 10.19350 | 11.66090 |
| C | -4.37530 | 11.03090 | 12.69560 |
| H | -3.64560 | 11.07070 | 13.50420 |
| H | -5.30820 | 10.65810 | 13.11740 |
| H | -4.53280 | 12.04960 | 12.33980 |
| C | -4.63760 | 9.26290 | 8.10750 |
| H | -3.36390 | 8.64930 | 9.68850 |
| C | -2.70290 | 10.56490 | 9.01610 |
| H | -2.06800 | 10.74800 | 9.88380 |
| H | -3.09770 | 11.52630 | 8.68690 |
| H | -2.06450 | 10.17550 | 8.22270 |
| C | -4.73130 | 8.03840 | 7.56270 |
| H | -5.15330 | 10.09430 | 7.64800 |
| C | -5.53050 | 7.71190 | 6.31790 |
| H | -4.22090 | 7.20640 | 8.02770 |
| H | -5.94860 | 8.62360 | 5.89080 |
| H | -4.87260 | 7.27210 | 5.56870 |

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Compound **5.34**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -36.799282 kJ.

| | | | |
|---|---|---|---|
| O | -6.57130 | 6.31680 | 7.99680 |
| C | -6.89910 | 6.88320 | 6.82350 |
| O | -7.16980 | 6.27770 | 5.78810 |
| C | -6.50090 | 4.90040 | 8.10780 |
| H | -5.82420 | 4.63710 | 8.92080 |
| H | -6.04620 | 4.49310 | 7.20430 |
| C | -7.89900 | 4.27990 | 8.35400 |
| O | -7.95200 | 2.98540 | 7.76550 |
| H | -8.67020 | 4.90370 | 7.89760 |
| C | -8.23460 | 4.11580 | 9.85400 |
| C | -8.22350 | 2.99050 | 6.37020 |
| H | -9.18950 | 3.45000 | 6.15720 |
| H | -8.25730 | 1.96450 | 6.00410 |
| H | -7.45650 | 3.51810 | 5.80340 |
| C | -9.65950 | 3.57730 | 10.05950 |
| C | -8.05890 | 5.41790 | 10.61410 |
| H | -7.53950 | 3.38770 | 10.27510 |
| H | -10.40630 | 4.25590 | 9.64650 |
| H | -9.88020 | 3.44110 | 11.11850 |
| H | -9.78780 | 2.60970 | 9.57310 |
| C | -7.25690 | 5.57330 | 11.68040 |
| H | -8.60620 | 6.26790 | 10.23110 |
| H | -6.69020 | 4.73240 | 12.05450 |
| C | -7.02880 | 6.89290 | 12.39050 |
| C | -5.59440 | 7.37490 | 12.18360 |
| H | -7.22420 | 6.77330 | 13.45620 |
| H | -7.71490 | 7.65010 | 12.01180 |
| O | -4.87620 | 7.66310 | 13.13910 |
| O | -5.24510 | 7.46270 | 10.88940 |
| C | -3.94200 | 7.90810 | 10.53290 |
| C | -3.85430 | 9.45480 | 10.52090 |
| H | -3.21630 | 7.48090 | 11.22550 |
| H | -3.68180 | 7.50900 | 9.55250 |
| H | -4.55950 | 9.87460 | 11.24110 |
| C | -4.15550 | 10.06900 | 9.13470 |
| O | -2.53840 | 9.85660 | 10.88380 |
| C | -2.30050 | 9.87530 | 12.28500 |
| H | -2.42060 | 8.89050 | 12.73630 |
| H | -2.97030 | 10.57220 | 12.79030 |
| H | -1.27830 | 10.20270 | 12.47450 |
| C | -5.48100 | 9.57960 | 8.58000 |
| H | -3.36900 | 9.75000 | 8.44880 |
| C | -4.14220 | 11.60530 | 9.18140 |
| H | -3.17480 | 11.97980 | 9.51790 |
| H | -4.90070 | 11.99070 | 9.86320 |
| H | -4.33100 | 12.03100 | 8.19550 |
| C | -5.62790 | 8.96110 | 7.39670 |
| H | -6.34350 | 9.72600 | 9.21490 |
| C | -6.94170 | 8.40870 | 6.88060 |
| H | -4.76560 | 8.79230 | 6.76720 |
| H | -7.76220 | 8.71610 | 7.52860 |
| H | -7.13990 | 8.80650 | 5.88520 |

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Compound **5.34**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1154.07670090 hartree.
Free Energy: -1153.686264 hartree.

| | | | |
|---|---|---|---|
| O | -2.56429 | -1.41305 | -0.85228 |
| C | -1.69864 | -2.32158 | -0.34480 |
| O | -1.86145 | -2.92096 | 0.69635 |
| C | -3.74555 | -1.11781 | -0.07956 |
| H | -3.92685 | -1.94375 | 0.61079 |
| H | -4.56743 | -1.07036 | -0.79887 |
| C | -3.63994 | 0.20739 | 0.68934 |
| O | -2.58229 | 0.21278 | 1.62767 |
| H | -4.60778 | 0.29855 | 1.21958 |
| C | -3.48630 | 1.49450 | -0.16502 |
| C | -2.80587 | -0.55295 | 2.80106 |
| H | -1.98496 | -0.31674 | 3.48336 |
| H | -2.79566 | -1.63062 | 2.59944 |
| H | -3.75793 | -0.27689 | 3.28274 |
| C | -4.63866 | 1.65066 | -1.17535 |
| C | -2.14746 | 1.62083 | -0.85057 |
| H | -3.56042 | 2.31111 | 0.56485 |
| H | -5.61665 | 1.52133 | -0.69493 |
| H | -4.56371 | 0.92370 | -1.99250 |
| H | -4.61365 | 2.64889 | -1.62387 |
| C | -1.21350 | 2.51301 | -0.51650 |
| H | -1.96214 | 0.93848 | -1.67953 |
| H | -1.39100 | 3.18774 | 0.32159 |
| C | 0.11559 | 2.66245 | -1.21288 |
| C | 1.30827 | 2.32580 | -0.32414 |
| H | 0.27291 | 3.68889 | -1.56076 |
| H | 0.15196 | 1.99794 | -2.08544 |
| O | 2.23052 | 3.07680 | -0.08360 |

| | | | |
|---|---|---|---|
| O | 1.20831 | 1.06674 | 0.15432 |
| C | 2.27772 | 0.60303 | 1.00252 |
| C | 3.41487 | -0.04673 | 0.19203 |
| H | 2.66808 | 1.44386 | 1.57802 |
| H | 1.81517 | -0.12123 | 1.67666 |
| H | 3.58077 | 0.55429 | -0.71687 |
| C | 3.13095 | -1.51180 | -0.21133 |
| O | 4.59408 | -0.05178 | 0.99166 |
| C | 5.36868 | 1.13287 | 0.88329 |
| H | 4.77914 | 2.03688 | 1.08658 |
| H | 5.80994 | 1.22832 | -0.12058 |
| H | 6.17227 | 1.05297 | 1.62021 |
| C | 1.81140 | -1.64751 | -0.92779 |
| H | 3.08420 | -2.08683 | 0.72417 |
| C | 4.28300 | -2.06832 | -1.06869 |
| H | 5.23790 | -1.94462 | -0.55059 |
| H | 4.34332 | -1.54543 | -2.03218 |
| H | 4.12940 | -3.13228 | -1.27662 |
| C | 0.79548 | -2.41567 | -0.53031 |
| H | 1.70924 | -1.07004 | -1.84906 |
| C | -0.51193 | -2.53772 | -1.27164 |
| H | 0.87036 | -2.99791 | 0.38724 |
| H | -0.55937 | -1.84495 | -2.11535 |
| H | -0.62492 | -3.55819 | -1.66906 |

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Compound **5.34**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1154.08002502 hartree.
Free Energy: -1153.691966 hartree.

| | | | |
|---|---|---|---|
| O | 1.99283 | -1.27600 | 0.21280 |
| C | 1.23979 | -2.17779 | 0.88227 |
| O | 1.28440 | -2.33835 | 2.08153 |
| C | 2.84172 | -0.43800 | 1.02246 |
| H | 3.39417 | -1.06557 | 1.72677 |
| H | 2.21587 | 0.24647 | 1.60336 |
| C | 3.78838 | 0.33864 | 0.10856 |
| O | 4.70610 | -0.52781 | -0.54907 |
| H | 4.34389 | 1.03807 | 0.76074 |
| C | 3.07024 | 1.15735 | -0.99151 |
| C | 5.80052 | -0.94997 | 0.23988 |
| H | 5.49468 | -1.57446 | 1.09255 |
| H | 6.37549 | -0.09303 | 0.62541 |
| H | 6.44572 | -1.54601 | -0.41088 |
| C | 4.08987 | 1.95836 | -1.82235 |
| C | 2.02683 | 2.07410 | -0.40188 |
| H | 2.57328 | 0.43297 | -1.64709 |
| H | 4.59685 | 2.71078 | -1.20391 |
| H | 3.58758 | 2.48438 | -2.64085 |
| H | 4.84881 | 1.29395 | -2.24290 |
| C | 0.71914 | 2.01298 | -0.66567 |
| H | 2.39579 | 2.85131 | 0.27268 |
| H | 0.34165 | 1.24231 | -1.33611 |
| C | -0.32071 | 2.93141 | -0.07054 |
| C | -1.23981 | 2.17781 | 0.88225 |
| H | -0.93763 | 3.36865 | -0.86694 |
| H | 0.14472 | 3.74021 | 0.49783 |
| O | -1.28447 | 2.33843 | 2.08150 |
| O | -1.99280 | 1.27597 | 0.21280 |
| C | -2.84171 | 0.43800 | 1.02245 |
| C | -3.78837 | -0.33865 | 0.10856 |
| H | -2.21587 | -0.24648 | 1.60336 |
| H | -3.39415 | 1.06558 | 1.72676 |
| H | -4.34389 | -1.03807 | 0.76074 |
| C | -3.07024 | -1.15736 | -0.99150 |
| O | -4.70609 | 0.52781 | -0.54908 |
| C | -5.80049 | 0.94999 | 0.23987 |
| H | -5.49464 | 1.57452 | 1.09251 |
| H | -6.37545 | 0.09307 | 0.62545 |
| H | -6.44571 | 1.54600 | -0.41090 |
| C | -2.02683 | -2.07412 | -0.40187 |
| H | -2.57328 | -0.43300 | -1.64709 |
| C | -4.08987 | -1.95838 | -1.82234 |
| H | -4.84881 | -1.29397 | -2.24289 |
| H | -4.59685 | -2.71079 | -1.20389 |
| H | -3.58759 | -2.48440 | -2.64084 |
| C | -0.71914 | -2.01300 | -0.66566 |
| H | -2.39579 | -2.85132 | 0.27270 |
| C | 0.32071 | -2.93141 | -0.07053 |
| H | -0.34165 | -1.24233 | -1.33611 |
| H | -0.14471 | -3.74021 | 0.49785 |
| H | 0.93765 | -3.36866 | -0.86691 |

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Compound **5.34**
This structure was assigned as correct.
B3LYP/6-31g(d)
SMD implicit solvation in carbontetrachloride was used.

Electronic Energy: -1154.09980850 hartree.
Free Energy: -1153.711165 hartree.

| | | | |
|---|---|---|---|
| O | 2.01992 | -1.32322 | 0.21475 |
| C | 1.20874 | -2.16527 | 0.88811 |
| O | 1.19628 | -2.27027 | 2.09624 |
| C | 2.86317 | -0.47284 | 1.02115 |
| H | 3.42879 | -1.09355 | 1.72180 |
| H | 2.23363 | 0.20452 | 1.60590 |
| C | 3.80116 | 0.31093 | 0.10521 |
| O | 4.72409 | -0.55609 | -0.54880 |
| H | 4.35176 | 1.01244 | 0.75739 |
| C | 3.07792 | 1.12875 | -0.99280 |
| C | 5.85471 | -0.90844 | 0.22582 |
| H | 5.59302 | -1.47876 | 1.13001 |
| H | 6.43138 | -0.02053 | 0.53002 |
| H | 6.48719 | -1.53893 | -0.40625 |
| C | 4.09333 | 1.93060 | -1.82721 |
| C | 2.04004 | 2.04704 | -0.39489 |
| H | 2.57598 | 0.40819 | -1.64892 |
| H | 4.60718 | 2.68143 | -1.21231 |
| H | 3.58777 | 2.45909 | -2.64278 |
| H | 4.84912 | 1.26751 | -2.25701 |
| C | 0.73379 | 2.00956 | -0.67192 |
| H | 2.41344 | 2.80467 | 0.29890 |
| H | 0.35197 | 1.25968 | -1.36343 |
| C | -0.29919 | 2.92901 | -0.06433 |
| C | -1.20874 | 2.16529 | 0.88809 |
| H | -0.91915 | 3.37562 | -0.85253 |
| H | 0.17537 | 3.73021 | 0.50727 |
| O | -1.19630 | 2.27031 | 2.09622 |
| O | -2.01992 | 1.32322 | 0.21474 |
| C | -2.86318 | 0.47286 | 1.02114 |
| C | -3.80115 | -0.31093 | 0.10520 |
| H | -2.23364 | -0.20449 | 1.60590 |
| H | -3.42879 | 1.09358 | 1.72178 |
| H | -4.35171 | -1.01248 | 0.75739 |
| C | -3.07789 | -1.12872 | -0.99281 |
| O | -4.72414 | 0.55603 | -0.54879 |
| C | -5.85475 | 0.90834 | 0.22585 |
| H | -5.59309 | 1.47878 | 1.12997 |
| H | -6.43131 | 0.02040 | 0.53016 |
| H | -6.48734 | 1.53869 | -0.40626 |
| C | -2.04002 | -2.04702 | -0.39491 |
| H | -2.57595 | -0.40814 | -1.64890 |
| C | -4.09329 | -1.93055 | -1.82726 |
| H | -4.84908 | -1.26746 | -2.25704 |
| H | -4.60712 | -2.68141 | -1.21238 |
| H | -3.58771 | -2.45901 | -2.64285 |
| C | -0.73377 | -2.00956 | -0.67193 |
| H | -2.41343 | -2.80465 | 0.29889 |
| C | 0.29919 | -2.92901 | -0.06431 |
| H | -0.35193 | -1.25969 | -1.36344 |
| H | -0.17538 | -3.73020 | 0.50730 |
| H | 0.91917 | -3.37564 | -0.85249 |

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Compound **5.34**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1154.07699877 hartree.
Free Energy: -1153.686029 hartree.

| | | | |
|---|---|---|---|
| O | 1.56799 | -0.92096 | 0.14450 |
| C | 1.62300 | -2.24915 | -0.09889 |
| O | 2.29640 | -3.04066 | 0.52440 |
| C | 2.36875 | -0.38716 | 1.21244 |
| H | 2.69477 | -1.20299 | 1.86007 |
| H | 1.71187 | 0.28129 | 1.77467 |
| C | 3.55900 | 0.40069 | 0.65699 |
| O | 4.50763 | -0.43547 | 0.01215 |
| H | 4.03206 | 0.90303 | 1.52268 |
| C | 3.15304 | 1.46369 | -0.39354 |
| C | 5.26157 | -1.28028 | 0.86616 |
| H | 5.71525 | -0.71253 | 1.69411 |
| H | 6.05964 | -1.70685 | 0.25261 |
| H | 4.65718 | -2.10026 | 1.27341 |
| C | 4.35796 | 2.35141 | -0.75441 |
| C | 1.97692 | 2.30021 | 0.04707 |
| H | 2.85566 | 0.89853 | -1.28447 |
| H | 4.10505 | 3.03101 | -1.57498 |
| H | 5.20791 | 1.73463 | -1.05800 |
| H | 4.66689 | 2.96384 | 0.10297 |
| C | 0.78779 | 2.30165 | -0.56100 |
| H | 2.14089 | 2.95841 | 0.90457 |
| H | 0.62269 | 1.64720 | -1.41434 |
| C | -0.37079 | 3.17750 | -0.16719 |
| C | -1.70495 | 2.47100 | 0.03238 |
| H | -0.55470 | 3.92110 | -0.96030 |
| H | -0.16370 | 3.73631 | 0.74931 |
| O | -2.50557 | 2.76539 | 0.89374 |
| O | -1.92794 | 1.52879 | -0.91492 |

| | | | |
|---|---|---|---|
| C | -3.25219 | 0.94673 | -0.93828 |
| C | -3.45183 | -0.24468 | 0.02645 |
| H | -3.97678 | 1.72320 | -0.68877 |
| H | -3.40194 | 0.63906 | -1.97647 |
| H | -2.83649 | -0.08601 | 0.92432 |
| C | -3.11070 | -1.62664 | -0.58898 |
| O | -4.83451 | -0.27919 | 0.37241 |
| C | -5.16889 | 0.50129 | 1.51166 |
| H | -4.84608 | 1.54495 | 1.41009 |
| H | -4.71267 | 0.08586 | 2.42293 |
| H | -6.25717 | 0.46333 | 1.60854 |
| C | -1.67854 | -1.68126 | -1.07441 |
| H | -3.76365 | -1.71653 | -1.47369 |
| C | -3.47952 | -2.75739 | 0.37893 |
| H | -4.53045 | -2.67760 | 0.66192 |
| H | -2.87390 | -2.71226 | 1.29265 |
| H | -3.31730 | -3.73647 | -0.08382 |
| C | -0.76473 | -2.59153 | -0.72571 |
| H | -1.38376 | -0.90239 | -1.77790 |
| C | 0.66142 | -2.60539 | -1.22571 |
| H | -1.01482 | -3.38041 | -0.01952 |
| H | 0.94138 | -3.60084 | -1.58482 |
| H | 0.78629 | -1.88395 | -2.03971 |

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Compound **5.34**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
SMD implicit solvation in carbontetrachloride was used.

Electronic Energy: -1154.09509993 hartree.
Free Energy: -1153.704590 hartree.

| | | | |
|---|---|---|---|
| O | 1.59173 | -0.93467 | 0.16565 |
| C | 1.62323 | -2.26163 | -0.07394 |
| O | 2.28077 | -3.06484 | 0.55404 |
| C | 2.41086 | -0.39886 | 1.22067 |
| H | 2.75779 | -1.21316 | 1.85926 |
| H | 1.76111 | 0.25840 | 1.80420 |
| C | 3.58135 | 0.39976 | 0.64242 |
| O | 4.52186 | -0.43485 | -0.02230 |
| H | 4.06830 | 0.90206 | 1.49904 |
| C | 3.15104 | 1.46301 | -0.39873 |
| C | 5.31492 | -1.25294 | 0.82188 |
| H | 5.80571 | -0.66367 | 1.61270 |
| H | 6.08668 | -1.69930 | 0.18765 |
| H | 4.73626 | -2.06341 | 1.28364 |
| C | 4.34293 | 2.36416 | -0.76862 |
| C | 1.97354 | 2.28802 | 0.06080 |
| H | 2.84852 | 0.90163 | -1.29042 |
| H | 4.07722 | 3.04340 | -1.58618 |
| H | 5.19803 | 1.75946 | -1.08431 |
| H | 4.65599 | 2.97871 | 0.08582 |
| C | 0.78639 | 2.30925 | -0.55187 |
| H | 2.13522 | 2.92168 | 0.93679 |
| H | 0.62462 | 1.68232 | -1.42654 |
| C | -0.37053 | 3.17706 | -0.13620 |
| C | -1.70854 | 2.47537 | 0.04787 |
| H | -0.55376 | 3.94103 | -0.91004 |
| H | -0.15944 | 3.71353 | 0.79284 |
| O | -2.51758 | 2.78103 | 0.89927 |
| O | -1.92685 | 1.53000 | -0.89429 |
| C | -3.25376 | 0.95129 | -0.93452 |
| C | -3.46696 | -0.24525 | 0.01999 |
| H | -3.97826 | 1.72961 | -0.69006 |
| H | -3.39551 | 0.65265 | -1.97664 |
| H | -2.86925 | -0.09204 | 0.93034 |
| C | -3.11666 | -1.62525 | -0.59585 |
| O | -4.85773 | -0.28089 | 0.34022 |
| C | -5.21190 | 0.48990 | 1.47988 |
| H | -4.88189 | 1.53355 | 1.39926 |
| H | -4.78415 | 0.06198 | 2.39954 |
| H | -6.30330 | 0.46322 | 1.55192 |
| C | -1.67969 | -1.67852 | -1.06762 |
| H | -3.75849 | -1.71094 | -1.48861 |
| C | -3.49648 | -2.76023 | 0.36222 |
| H | -4.55347 | -2.68954 | 0.62701 |
| H | -2.91042 | -2.71797 | 1.28890 |
| H | -3.32371 | -3.73791 | -0.10061 |
| C | -0.76583 | -2.58452 | -0.70649 |
| H | -1.38281 | -0.90491 | -1.77611 |
| C | 0.66154 | -2.60473 | -1.20377 |
| H | -1.01799 | -3.36913 | 0.00389 |
| H | 0.93257 | -3.60122 | -1.56757 |
| H | 0.79419 | -1.88176 | -2.01505 |

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Compound **5.34**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in carbontetrachloride was used.

Electronic Energy: -1153.61073369 hartree.
Free Energy: -1153.216705 hartree.

| | | | |
|---|---|---|---|
| O | 2.00329 | -1.25341 | 0.23172 |
| C | 1.21220 | -2.09444 | 0.91621 |
| O | 1.21871 | -2.18844 | 2.11879 |
| C | 2.86032 | -0.42478 | 1.02335 |
| H | 3.42737 | -1.05368 | 1.71637 |
| H | 2.25052 | 0.26528 | 1.61506 |
| C | 3.78883 | 0.32917 | 0.08333 |
| O | 4.68746 | -0.55474 | -0.55693 |
| H | 4.35279 | 1.05328 | 0.69950 |
| C | 3.04247 | 1.09805 | -1.01859 |
| C | 5.81015 | -0.89367 | 0.22066 |
| H | 5.53979 | -1.42856 | 1.14169 |
| H | 6.39110 | -0.00057 | 0.49349 |
| H | 6.43623 | -1.54938 | -0.38856 |
| C | 4.03467 | 1.88014 | -1.88349 |
| C | 2.01750 | 2.01963 | -0.41756 |
| H | 2.53071 | 0.35198 | -1.63810 |
| H | 4.55461 | 2.64031 | -1.28729 |
| H | 3.51459 | 2.39207 | -2.69835 |
| H | 4.78283 | 1.20846 | -2.31045 |
| C | 0.70698 | 1.94478 | -0.63960 |
| H | 2.40228 | 2.80399 | 0.24015 |
| H | 0.31191 | 1.16727 | -1.29285 |
| C | -0.30747 | 2.86923 | -0.01871 |
| C | -1.21215 | 2.09440 | 0.91620 |
| H | -0.92972 | 3.32913 | -0.79528 |
| H | 0.18105 | 3.65340 | 0.56274 |
| O | -1.21836 | 2.18805 | 2.11880 |
| O | -2.00338 | 1.25353 | 0.23166 |
| C | -2.86025 | 0.42471 | 1.02329 |
| C | -3.78883 | -0.32919 | 0.08330 |
| H | -2.25032 | -0.26538 | 1.61482 |
| H | -3.42724 | 1.05349 | 1.71647 |
| H | -4.35260 | -1.05345 | 0.69948 |
| C | -3.04252 | -1.09796 | -1.01876 |
| O | -4.68763 | 0.55464 | -0.55676 |
| C | -5.81018 | 0.89356 | 0.22106 |
| H | -5.53963 | 1.42864 | 1.14191 |
| H | -6.39095 | 0.00043 | 0.49417 |
| H | -6.43647 | 1.54909 | -0.38813 |
| C | -2.01756 | -2.01961 | -0.41782 |
| H | -2.53075 | -0.35185 | -1.63821 |
| C | -4.03472 | -1.87996 | -1.88372 |
| H | -4.78282 | -1.20822 | -2.31072 |
| H | -4.55476 | -2.64010 | -1.28756 |
| H | -3.51464 | -2.39192 | -2.69855 |
| C | -0.70699 | -1.94454 | -0.63953 |
| H | -2.40241 | -2.80421 | 0.23958 |
| C | 0.30741 | -2.86911 | -0.01873 |
| H | -0.31186 | -1.16677 | -1.29241 |
| H | -0.18114 | -3.65330 | 0.56266 |
| H | 0.92961 | -3.32898 | -0.79536 |

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Compound **5.34**
This structure was assigned as incorrect.
M06-2X/6-31g(d)
SMD implicit solvation in carbontetrachloride was used.

Electronic Energy: -1153.60986926 hartree.
Free Energy: -1153.211088 hartree.

| | | | |
|---|---|---|---|
| O | -1.96728 | 1.24220 | 0.16605 |
| C | -1.24758 | 2.16045 | 0.83064 |
| O | -1.35135 | 2.36159 | 2.01524 |
| C | -2.87029 | 0.46529 | 0.95879 |
| H | -3.47701 | 1.13475 | 1.57556 |
| H | -2.29624 | -0.18289 | 1.62877 |
| C | -3.74170 | -0.35181 | 0.01659 |
| O | -4.61012 | 0.48539 | -0.72092 |
| H | -4.33276 | -1.04489 | 0.64256 |
| C | -2.93232 | -1.17358 | -0.99850 |
| C | -5.77678 | 0.85421 | -0.02582 |
| H | -6.37218 | -0.02803 | 0.25101 |
| H | -6.36677 | 1.48231 | -0.69699 |
| H | -5.56019 | 1.42890 | 0.88536 |
| C | -3.87254 | -2.02863 | -1.85279 |
| C | -1.91945 | -2.03419 | -0.29558 |
| H | -2.40836 | -0.45696 | -1.64200 |
| H | -3.31404 | -2.56201 | -2.62749 |
| H | -4.62789 | -1.40142 | -2.33197 |
| H | -4.38698 | -2.77490 | -1.23484 |
| C | -0.60199 | -1.95477 | -0.46961 |
| H | -2.31964 | -2.77938 | 0.39721 |
| H | -0.18958 | -1.21743 | -1.15760 |
| C | 0.39499 | -2.82313 | 0.25238 |
| C | 1.26244 | -1.97796 | 1.16069 |
| H | 1.04621 | -3.33504 | -0.46587 |
| H | -0.11031 | -3.56623 | 0.87230 |
| O | 1.21419 | -1.97123 | 2.36500 |

| | | | |
|---|---|---|---|
| O | 2.09512 | -1.19949 | 0.44661 |
| C | 2.93446 | -0.32515 | 1.21514 |
| C | 3.85098 | 0.45910 | 0.28401 |
| H | 3.53049 | -0.91645 | 1.91746 |
| H | 2.29860 | 0.35561 | 1.78906 |
| H | 4.26189 | 1.27775 | 0.89103 |
| C | 3.10483 | 1.09434 | -0.90790 |
| O | 4.99829 | -0.26974 | -0.11054 |
| C | 4.76108 | -1.45098 | -0.84587 |
| H | 4.11466 | -1.28108 | -1.71658 |
| H | 4.31295 | -2.23905 | -0.22793 |
| H | 5.73632 | -1.79537 | -1.19833 |
| C | 2.05320 | 2.03900 | -0.39365 |
| H | 2.59979 | 0.30424 | -1.47552 |
| C | 4.09495 | 1.82109 | -1.82132 |
| H | 4.84262 | 1.13061 | -2.22088 |
| H | 4.62798 | 2.60504 | -1.27008 |
| H | 3.57097 | 2.29286 | -2.65767 |
| C | 0.74779 | 1.92187 | -0.62777 |
| H | 2.41408 | 2.87766 | 0.20835 |
| C | -0.29178 | 2.87578 | -0.10080 |
| H | 0.37755 | 1.09007 | -1.22642 |
| H | 0.17174 | 3.69158 | 0.45704 |
| H | -0.87649 | 3.29447 | -0.92893 |

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Compound **5.35**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -63.616680 kJ.

| | | | |
|---|---|---|---|
| O | 3.69180 | 5.32190 | -6.33590 |
| C | 3.74810 | 5.11420 | -7.65650 |
| O | 3.54980 | 4.04310 | -8.22580 |
| C | 3.25460 | 4.27060 | -5.49200 |
| H | 3.75100 | 3.33000 | -5.73650 |
| H | 2.19220 | 4.12210 | -5.68410 |
| C | 3.50790 | 4.64130 | -4.01400 |
| C | 2.37170 | 4.15530 | -3.08130 |
| C | 1.01740 | 4.77410 | -3.43850 |
| C | 0.02830 | 4.01420 | -3.95390 |
| C | -1.34770 | 4.47870 | -4.39810 |
| C | -1.31480 | 4.87510 | -5.87070 |
| H | -1.69380 | 5.32090 | -3.80170 |
| H | -2.06590 | 3.67200 | -4.25250 |
| O | -1.78740 | 4.14750 | -6.74140 |
| O | -0.72360 | 6.05710 | -6.07630 |
| C | -0.61240 | 6.55500 | -7.39890 |
| C | -0.05090 | 7.99510 | -7.38150 |
| H | 0.05720 | 5.88410 | -7.93660 |
| H | -1.57360 | 6.52800 | -7.91440 |
| C | 0.63880 | 8.37870 | -8.71580 |
| C | 1.79100 | 7.43810 | -9.05810 |
| C | 2.88210 | 7.34560 | -8.27000 |
| C | 4.04810 | 6.38870 | -8.43640 |
| H | 2.92760 | 7.94610 | -7.37310 |
| H | 4.21950 | 6.14610 | -9.48380 |
| H | 4.96070 | 6.84930 | -8.05930 |
| H | 0.21610 | 2.96540 | -4.13480 |
| C | 1.58700 | 6.61280 | -10.31920 |
| H | 1.52360 | 7.26880 | -11.18780 |
| H | 0.65690 | 6.04760 | -10.25560 |
| H | 2.38550 | 5.89580 | -10.50100 |
| C | 0.87520 | 6.27220 | -3.18910 |
| H | -0.09340 | 6.66600 | -3.48890 |
| H | 1.62550 | 6.83030 | -3.74770 |
| H | 0.99720 | 6.50070 | -2.13070 |
| H | 2.29000 | 3.07590 | -3.21930 |
| C | 2.70590 | 4.37830 | -1.59410 |
| H | 1.87600 | 4.07910 | -0.95350 |
| H | 2.93780 | 5.42210 | -1.38290 |
| H | 3.57340 | 3.78900 | -1.29550 |
| H | 3.59970 | 5.72290 | -3.90400 |
| O | 4.71220 | 4.02030 | -3.57480 |
| C | 5.89970 | 4.62990 | -4.05970 |
| H | 6.76560 | 4.12730 | -3.62860 |
| H | 5.95040 | 5.68200 | -3.77640 |
| H | 5.98200 | 4.55420 | -5.14410 |
| H | -0.10910 | 8.28820 | -9.50540 |
| C | 1.11900 | 9.84250 | -8.72160 |
| H | 1.61490 | 10.08880 | -9.66090 |
| H | 1.81880 | 10.04290 | -7.91050 |
| H | 0.28160 | 10.53160 | -8.60840 |
| H | 0.68060 | 8.09810 | -6.57800 |
| O | -1.11360 | 8.92700 | -7.19890 |
| C | -1.58220 | 9.04850 | -5.86410 |
| H | -2.08270 | 8.14260 | -5.52380 |
| H | -2.30800 | 9.85980 | -5.81100 |
| H | -0.77040 | 9.28350 | -5.17460 |

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Compound **5.35**
This structure was assigned as incorrect.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -52.003632 kJ.

| | | | |
|---|---|---|---|
| O | 3.16470 | 5.54720 | -5.90400 |
| C | 4.03650 | 6.09140 | -6.76630 |
| O | 5.00480 | 6.78970 | -6.46960 |
| C | 3.32130 | 5.73090 | -4.50420 |
| H | 2.38890 | 6.14460 | -4.12020 |
| H | 4.08450 | 6.47010 | -4.26160 |
| C | 3.61880 | 4.37990 | -3.81170 |
| C | 2.55240 | 3.29080 | -4.09180 |
| C | 1.12090 | 3.80380 | -3.93110 |
| C | 0.32570 | 3.95570 | -5.00970 |
| C | -1.08230 | 4.52560 | -5.04020 |
| C | -1.03690 | 6.04230 | -5.22070 |
| H | -1.61880 | 4.28610 | -4.12320 |
| H | -1.64030 | 4.07840 | -5.86230 |
| O | -1.70870 | 6.78880 | -4.51030 |
| O | -0.20350 | 6.42650 | -6.19930 |
| C | -0.04300 | 7.80230 | -6.51430 |
| C | -0.55080 | 8.09220 | -7.94660 |
| H | -0.52630 | 8.45720 | -5.78970 |
| H | 1.01980 | 8.03380 | -6.44600 |
| C | 0.12100 | 7.21470 | -9.03300 |
| C | 1.64100 | 7.14070 | -8.88330 |
| C | 2.23350 | 5.99210 | -8.49780 |
| C | 3.71100 | 5.76790 | -8.22390 |
| H | 1.61100 | 5.13770 | -8.27360 |
| H | 3.96810 | 4.72960 | -8.43180 |
| H | 4.32530 | 6.38550 | -8.87760 |
| H | 0.72940 | 3.73170 | -5.98680 |
| C | 2.40980 | 8.42470 | -9.16690 |
| H | 3.46550 | 8.35130 | -8.91090 |
| H | 2.00140 | 9.25490 | -8.59190 |
| H | 2.34670 | 8.68050 | -10.22440 |
| C | 0.68210 | 4.14450 | -2.51290 |
| H | -0.28970 | 4.63430 | -2.47660 |
| H | 1.39440 | 4.81900 | -2.03920 |
| H | 0.61580 | 3.24070 | -1.90740 |
| H | 2.67390 | 3.00120 | -5.13700 |
| C | 2.79540 | 2.01900 | -3.26010 |
| H | 2.04120 | 1.26050 | -3.47100 |
| H | 2.77710 | 2.22460 | -2.18990 |
| H | 3.76880 | 1.58490 | -3.49070 |
| H | 3.65590 | 4.55100 | -2.73460 |
| O | 4.87670 | 3.85890 | -4.23330 |
| C | 6.01230 | 4.54440 | -3.72580 |
| H | 6.91650 | 4.02790 | -4.04760 |
| H | 6.01120 | 4.56310 | -2.63530 |
| H | 6.07380 | 5.56760 | -4.09570 |
| H | -0.26450 | 6.20310 | -8.89480 |
| C | -0.28800 | 7.64300 | -10.45340 |
| H | -0.01770 | 8.67870 | -10.65830 |
| H | -1.36650 | 7.55570 | -10.58930 |
| H | 0.18800 | 7.01460 | -11.20650 |
| H | -0.34090 | 9.13810 | -8.17610 |
| O | -1.95710 | 7.87940 | -8.04010 |
| C | -2.75800 | 8.85540 | -7.38970 |
| H | -2.61790 | 8.84790 | -6.30900 |
| H | -3.80960 | 8.64280 | -7.58210 |
| H | -2.54800 | 9.85740 | -7.76550 |

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Compound **5.35**
This structure was assigned as incorrect.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1232.70472893 hartree.
Free Energy: -1232.263513 hartree.

| | | | |
|---|---|---|---|
| O | -1.03628 | 2.14989 | -0.00504 |
| C | -0.16912 | 2.65344 | 0.90468 |
| O | -0.32627 | 2.56966 | 2.10286 |
| C | -2.14404 | 1.39015 | 0.53474 |
| H | -2.79664 | 2.05453 | 1.10969 |
| H | -1.73903 | 0.63074 | 1.20756 |
| C | -2.92097 | 0.76528 | -0.62566 |
| C | -3.78089 | -0.43137 | -0.14417 |
| C | -2.92647 | -1.54527 | 0.47226 |
| C | -1.97591 | -2.15776 | -0.25109 |
| C | -1.04783 | -3.26053 | 0.22221 |
| C | 0.16913 | -2.65348 | 0.90468 |
| H | -0.72045 | -3.85768 | -0.63510 |
| H | -1.52921 | -3.92519 | 0.94206 |
| O | 0.32631 | -2.56974 | 2.10286 |
| O | 1.03627 | -2.14990 | -0.00504 |
| C | 2.14406 | -1.39022 | 0.53475 |
| C | 2.92094 | -0.76526 | -0.62564 |
| H | 1.73908 | -0.63085 | 1.20764 |
| H | 2.79668 | -2.05464 | 1.10963 |
| C | 3.78088 | 0.43136 | -0.14412 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.92649 | 1.54530 | 0.47226 | | | | |
| C | 1.97594 | 2.15778 | -0.25110 | O | -1.29439 | 2.05710 | 0.01672 |
| C | 1.04782 | 3.26052 | 0.22220 | C | -0.37291 | 2.62571 | 0.82164 |
| H | 1.80200 | 1.82871 | -1.27394 | O | -0.38412 | 2.52495 | 2.03276 |
| H | 1.52918 | 3.92519 | 0.94205 | C | -2.24348 | 1.16579 | 0.65746 |
| H | 0.72042 | 3.85767 | -0.63510 | H | -2.84394 | 1.72150 | 1.38394 |
| H | -1.80198 | -1.82871 | -1.27394 | H | -1.67624 | 0.39944 | 1.18924 |
| C | 3.24959 | 1.89109 | 1.90508 | C | -3.14997 | 0.55504 | -0.41701 |
| H | 4.29586 | 2.21461 | 1.99755 | C | -3.57106 | -0.89434 | -0.03831 |
| H | 3.14236 | 1.00566 | 2.54618 | C | -2.37942 | -1.85035 | -0.10337 |
| H | 2.60470 | 2.66813 | 2.31972 | C | -1.84753 | -2.32967 | 1.03404 |
| C | -3.24962 | -1.89107 | 1.90506 | C | -0.66223 | -3.26552 | 1.17159 |
| H | -2.60475 | -2.66811 | 2.31972 | C | 0.57250 | -2.46295 | 1.55273 |
| H | -4.29589 | -2.21460 | 1.99749 | H | -0.46976 | -3.82216 | 0.25202 |
| H | -3.14242 | -1.00565 | 2.54617 | H | -0.84643 | -3.98050 | 1.97938 |
| H | -4.44335 | -0.04255 | 0.64185 | O | 0.92787 | -2.22666 | 2.69030 |
| C | -4.67848 | -0.96406 | -1.27621 | O | 1.20391 | -1.98554 | 0.45941 |
| H | -5.29026 | -1.79876 | -0.91686 | C | 2.30695 | -1.07376 | 0.69858 |
| H | -4.07665 | -1.33135 | -2.11575 | C | 2.84314 | -0.59593 | -0.65268 |
| H | -5.33896 | -0.17682 | -1.64645 | H | 1.93171 | -0.24311 | 1.30063 |
| H | -2.19799 | 0.40926 | -1.37655 | H | 3.09269 | -1.58958 | 1.25880 |
| O | -3.80523 | 1.70428 | -1.22582 | C | 3.64494 | 0.72393 | -0.51005 |
| C | -3.21803 | 2.59241 | -2.16132 | C | 2.80534 | 1.85037 | 0.10568 |
| H | -4.04201 | 3.13081 | -2.63801 | C | 1.67835 | 2.26835 | -0.49394 |
| H | -2.65492 | 2.04630 | -2.93422 | C | 0.71078 | 3.32067 | 0.01351 |
| H | -2.54252 | 3.31443 | -1.68639 | H | 1.36566 | 1.78069 | -1.41568 |
| H | 4.44330 | 0.04251 | 0.64192 | H | 1.19317 | 4.05450 | 0.66142 |
| C | 4.67854 | 0.96399 | -1.27614 | H | 0.25402 | 3.84501 | -0.83223 |
| H | 4.07676 | 1.33134 | -2.11569 | H | -2.27304 | -2.00392 | 1.98288 |
| H | 5.33895 | 0.17669 | -1.64639 | C | 3.35016 | 2.41844 | 1.39158 |
| H | 5.29039 | 1.79862 | -0.91677 | H | 2.75458 | 3.24145 | 1.79293 |
| H | 2.19794 | -0.40919 | -1.37649 | H | 4.37921 | 2.77646 | 1.24734 |
| O | 3.80520 | -1.70419 | -1.22590 | H | 3.40057 | 1.63832 | 2.16381 |
| C | 3.21800 | -2.59228 | -2.16143 | C | -1.87945 | -2.22859 | -1.47975 |
| H | 2.54254 | -3.31436 | -1.68653 | H | -1.82931 | -1.35691 | -2.14282 |
| H | 4.04198 | -3.13061 | -2.63821 | H | -2.55640 | -2.94692 | -1.96149 |
| H | 2.65482 | -2.04614 | -2.93427 | H | -0.88264 | -2.67327 | -1.45252 |
| --- | | | | H | -3.92130 | -0.86408 | 1.00241 |
| | | | | C | -4.73963 | -1.38399 | -0.91342 |
| Compound **5.35** | | | | H | -4.99723 | -2.41866 | -0.65921 |
| This structure was assigned as incorrect. | | | | H | -4.49167 | -1.34896 | -1.98052 |
| B3LYP/6-31g(d) | | | | H | -5.62327 | -0.76118 | -0.75756 |
| SMD implicit solvation in dichloromethane was used. | | | | H | -2.59603 | 0.53725 | -1.36807 |
| | | | | O | -4.34073 | 1.31841 | -0.59047 |
| | | | | C | -4.15432 | 2.56773 | -1.23681 |
| Electronic Energy: -1232.72786172 hartree. | | | | H | -5.15143 | 2.98506 | -1.40785 |
| | | | | H | -3.64530 | 2.44953 | -2.20601 |
| Free Energy: -1232.286547 hartree. | | | | H | -3.57766 | 3.27645 | -0.62663 |

| | | | |
|---|---|---|---|
| H | 4.47202 | 0.51152 | 0.18090 |
| C | 4.26276 | 1.14656 | -1.85489 |
| H | 3.48563 | 1.33007 | -2.60657 |
| H | 4.93094 | 0.37045 | -2.23755 |
| H | 4.83834 | 2.07195 | -1.73738 |
| H | 1.98932 | -0.42934 | -1.32728 |
| O | 3.72587 | -1.55208 | -1.23510 |
| C | 3.10853 | -2.67495 | -1.84624 |
| H | 2.68783 | -3.37520 | -1.11330 |
| H | 3.88937 | -3.18937 | -2.41549 |
| H | 2.30857 | -2.37106 | -2.53833 |

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Compound **5.35**
This structure was assigned as correct.
B3LYP/6-31g(d)
Gas phase.

Electronic Energy: -1232.70827713 hartree.
Free Energy: -1232.265477 hartree.

| | | | |
|---|---|---|---|
| O | -2.02901 | -2.35780 | -0.93395 |
| C | -1.02484 | -2.97277 | -0.25831 |
| O | -1.04359 | -3.18766 | 0.93509 |
| C | -3.13071 | -1.86748 | -0.14009 |
| H | -3.27612 | -2.52565 | 0.71756 |
| H | -4.00532 | -1.91843 | -0.79163 |
| C | -2.86200 | -0.42545 | 0.32729 |
| C | -2.95727 | 0.59228 | -0.84054 |
| C | -2.14861 | 1.85665 | -0.57287 |
| C | -1.05213 | 2.10014 | -1.30842 |
| C | -0.13417 | 3.30107 | -1.18378 |
| C | 1.02484 | 2.97272 | -0.25833 |
| H | -0.65339 | 4.16606 | -0.76662 |
| H | 0.25774 | 3.56998 | -2.17001 |
| O | 1.04368 | 3.18774 | 0.93504 |
| O | 2.02898 | 2.35775 | -0.93401 |
| C | 3.13073 | 1.86747 | -0.14019 |
| C | 2.86203 | 0.42546 | 0.32726 |
| H | 4.00530 | 1.91839 | -0.79178 |
| H | 3.27619 | 2.52567 | 0.71743 |
| C | 2.95725 | -0.59232 | -0.84054 |
| C | 2.14854 | -1.85664 | -0.57285 |
| C | 1.05210 | -2.10015 | -1.30845 |
| C | 0.13415 | -3.30109 | -1.18380 |
| H | 0.75470 | -1.37289 | -2.06278 |
| H | -0.25778 | -3.57000 | -2.17002 |
| H | 0.65339 | -4.16608 | -0.76666 |
| H | -0.75468 | 1.37284 | -2.06269 |
| C | 2.64381 | -2.78724 | 0.51310 |
| H | 3.08091 | -2.21557 | 1.33633 |
| H | 3.43841 | -3.44632 | 0.13586 |
| H | 1.84411 | -3.41273 | 0.91554 |
| C | -2.64397 | 2.78726 | 0.51302 |
| H | -1.84438 | 3.41299 | 0.91530 |
| H | -3.08084 | 2.21560 | 1.33636 |
| H | -3.43877 | 3.44611 | 0.13580 |
| H | -2.48764 | 0.08769 | -1.69497 |
| C | -4.41740 | 0.90982 | -1.21837 |
| H | -4.44336 | 1.58141 | -2.08321 |
| H | -4.94911 | 1.38593 | -0.39098 |
| H | -4.96901 | 0.00163 | -1.48611 |
| H | -1.84151 | -0.39212 | 0.73708 |
| O | -3.80137 | -0.09159 | 1.34593 |
| C | -3.39884 | -0.48085 | 2.65142 |
| H | -4.23459 | -0.25491 | 3.31870 |
| H | -2.51305 | 0.08387 | 2.97842 |
| H | -3.16746 | -1.55256 | 2.71557 |
| H | 2.48766 | -0.08772 | -1.69499 |
| C | 4.41737 | -0.90994 | -1.21835 |
| H | 4.94903 | -1.38611 | -0.39096 |
| H | 4.96905 | -0.00178 | -1.48605 |
| H | 4.44331 | -1.58151 | -2.08320 |
| H | 1.84156 | 0.39215 | 0.73708 |
| O | 3.80143 | 0.09163 | 1.34588 |
| C | 3.39896 | 0.48096 | 2.65136 |
| H | 3.16756 | 1.55267 | 2.71546 |
| H | 4.23474 | 0.25507 | 3.31862 |
| H | 2.51319 | -0.08376 | 2.97843 |

---

Compound **5.35**
This structure was assigned as correct.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1232.21008119 hartree.
Free Energy: -1231.759613 hartree.

| | | | |
|---|---|---|---|
| O | -2.24586 | -1.55289 | -0.19638 |
| C | -0.98113 | -1.46274 | -0.64314 |
| O | -0.68205 | -1.09644 | -1.75329 |
| C | -3.28171 | -1.04042 | -1.04247 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -3.76492 | -1.88531 | -1.54367 | H | 4.49848 | 0.72991 | 0.83369 |
| H | -2.85290 | -0.38040 | -1.80089 | O | 5.46271 | 0.20525 | -0.92229 |
| C | -4.29206 | -0.28706 | -0.18126 | C | 6.37867 | 1.24037 | -0.63670 |
| C | -3.82957 | 1.13035 | 0.19741 | H | 5.92648 | 2.23581 | -0.74265 |
| C | -2.45258 | 1.14770 | 0.83549 | H | 7.19872 | 1.15148 | -1.35316 |
| C | -1.42001 | 1.68617 | 0.17563 | H | 6.77957 | 1.14396 | 0.38191 |
| C | -0.00522 | 1.79157 | 0.66803 | ---------- | | | |
| C | 1.00480 | 1.67589 | -0.45178 | | | | |
| H | 0.24613 | 1.03316 | 1.41609 | Compound **5.35** | | | |
| H | 0.17813 | 2.76351 | 1.15079 | This structure was assigned as incorrect. | | | |
| O | 0.77172 | 1.77614 | -1.63155 | M06-2X/6-31g(d) | | | |
| O | 2.23389 | 1.46899 | 0.04772 | SMD implicit solvation in dichloromethane | | | |
| C | 3.25847 | 1.10948 | -0.88361 | was used. | | | |
| C | 4.28267 | 0.25904 | -0.13903 | | | | |
| H | 2.82190 | 0.55072 | -1.71719 | Electronic Energy: -1232.20764604 har- | | | |
| H | 3.72272 | 2.01927 | -1.27913 | tree. | | | |
| C | 3.82596 | -1.19577 | 0.07552 | Free Energy: -1231.756643 hartree. | | | |
| C | 2.44968 | -1.29778 | 0.70994 | | | | |
| C | 1.41895 | -1.74402 | -0.01816 | O | -1.79055 | 1.48827 | 0.00813 |
| C | -0.00613 | -1.90309 | 0.42688 | C | -0.79459 | 2.31126 | -0.34524 |
| H | 1.60375 | -2.02630 | -1.05368 | O | -0.46123 | 2.50272 | -1.49352 |
| H | -0.24257 | -2.95203 | 0.65645 | C | -2.33020 | 0.68119 | -1.04836 |
| H | -0.24237 | -1.33749 | 1.33391 | H | -1.53351 | 0.03143 | -1.42157 |
| H | -1.59033 | 2.10027 | -0.81684 | H | -2.66233 | 1.32654 | -1.86701 |
| C | 2.35302 | -0.89163 | 2.15698 | C | -3.50012 | -0.12878 | -0.50357 |
| H | 2.81354 | 0.08937 | 2.31971 | C | -3.29317 | -0.65608 | 0.92369 |
| H | 2.88376 | -1.60732 | 2.79654 | C | -1.93073 | -1.28245 | 1.18083 |
| H | 1.32140 | -0.84252 | 2.51345 | C | -1.38959 | -2.14441 | 0.31369 |
| C | -2.35503 | 0.55936 | 2.21995 | C | -0.06078 | -2.84308 | 0.43407 |
| H | -1.32170 | 0.40155 | 2.53900 | C | 0.95999 | -2.29861 | -0.54706 |
| H | -2.87536 | -0.40345 | 2.27358 | H | -0.15891 | -3.91112 | 0.22224 |
| H | -2.82462 | 1.22135 | 2.95795 | H | 0.36482 | -2.73535 | 1.43620 |
| H | -3.76988 | 1.68384 | -0.74952 | O | 1.57142 | -2.96826 | -1.34632 |
| C | -4.88465 | 1.79632 | 1.08632 | O | 1.08364 | -0.96730 | -0.42336 |
| H | -4.58205 | 2.81330 | 1.35636 | C | 2.05768 | -0.31832 | -1.24805 |
| H | -5.03814 | 1.23012 | 2.01224 | C | 3.35182 | -0.11885 | -0.46645 |
| H | -5.84102 | 1.84694 | 0.55966 | H | 2.22920 | -0.91509 | -2.14606 |
| H | -4.49425 | -0.87142 | 0.73066 | H | 1.62097 | 0.64201 | -1.53186 |
| O | -5.48456 | -0.14414 | -0.93512 | C | 3.17245 | 0.70114 | 0.82813 |
| C | -6.40189 | -1.19867 | -0.73936 | C | 2.26284 | 1.89264 | 0.60238 |
| H | -6.77155 | -1.21363 | 0.29537 | C | 1.03724 | 1.88076 | 1.13783 |
| H | -7.24211 | -1.02713 | -1.41618 | C | -0.07247 | 2.86926 | 0.86124 |
| H | -5.96083 | -2.17887 | -0.96704 | H | 0.74989 | 1.02010 | 1.73805 |
| H | 3.76404 | -1.63422 | -0.92945 | H | -0.75664 | 2.93581 | 1.71031 |
| C | 4.89114 | -1.95433 | 0.87419 | H | 0.30006 | 3.86519 | 0.61743 |
| H | 5.06614 | -1.48366 | 1.84845 | H | -1.93447 | -2.36924 | -0.60457 |
| H | 5.83762 | -1.95925 | 0.32762 | C | 2.79267 | 2.99009 | -0.28325 |
| H | 4.58530 | -2.99120 | 1.04823 | H | 2.01806 | 3.69691 | -0.58470 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 3.23115 | 2.57432 | -1.19881 | C | -2.46732 | 1.44120 | 0.76349 |
| H | 3.59165 | 3.54651 | 0.22192 | C | -1.50423 | 2.03945 | 0.04313 |
| C | -1.31595 | -0.87054 | 2.48945 | C | -0.10054 | 2.37880 | 0.47774 |
| H | -0.34171 | -1.32351 | 2.68357 | C | 0.92152 | 1.96601 | -0.56924 |
| H | -1.98543 | -1.12893 | 3.32042 | H | 0.17002 | 1.94347 | 1.44058 |
| H | -1.19965 | 0.21970 | 2.50894 | H | 0.00525 | 3.47104 | 0.58225 |
| H | -3.37355 | 0.22835 | 1.56753 | O | 0.77645 | 2.09090 | -1.76955 |
| C | -4.42179 | -1.62133 | 1.30005 | O | 2.03506 | 1.46155 | -0.00313 |
| H | -4.32610 | -1.94737 | 2.34112 | C | 3.08128 | 1.04040 | -0.90987 |
| H | -4.39274 | -2.51381 | 0.66452 | C | 4.15518 | 0.29096 | -0.11237 |
| H | -5.39572 | -1.13891 | 1.17843 | H | 2.65282 | 0.40943 | -1.69317 |
| H | -3.65925 | -0.97128 | -1.19667 | H | 3.50946 | 1.92982 | -1.38170 |
| O | -4.67743 | 0.66412 | -0.45638 | C | 3.83302 | -1.20730 | 0.12322 |
| C | -5.38786 | 0.69007 | -1.67346 | C | 2.46743 | -1.44139 | 0.76348 |
| H | -6.25145 | 1.34374 | -1.52999 | C | 1.50415 | -2.03941 | 0.04319 |
| H | -5.74023 | -0.31409 | -1.94975 | C | 0.10044 | -2.37860 | 0.47789 |
| H | -4.78323 | 1.08608 | -2.50129 | H | 1.72873 | -2.32775 | -0.98248 |
| H | 2.67626 | 0.02639 | 1.53659 | H | -0.00545 | -3.47080 | 0.58273 |
| C | 4.54278 | 1.08413 | 1.39126 | H | -0.17013 | -1.94296 | 1.44058 |
| H | 5.09508 | 1.72317 | 0.69293 | H | -1.72904 | 2.32797 | -0.98244 |
| H | 5.13811 | 0.18374 | 1.56679 | C | 2.31124 | -1.01368 | 2.20424 |
| H | 4.44140 | 1.62297 | 2.33870 | H | 2.69572 | 0.00057 | 2.36195 |
| H | 4.06047 | 0.39886 | -1.13539 | H | 2.87746 | -1.67401 | 2.87474 |
| O | 3.89322 | -1.36363 | -0.06638 | H | 1.27082 | -1.02796 | 2.53854 |
| C | 4.59588 | -2.04152 | -1.08549 | C | -2.31077 | 1.01336 | 2.20420 |
| H | 3.95680 | -2.27333 | -1.94539 | H | -1.27008 | 1.02610 | 2.53773 |
| H | 4.95021 | -2.98180 | -0.65620 | H | -2.69662 | -0.00029 | 2.36230 |
| H | 5.46183 | -1.45488 | -1.42381 | H | -2.87551 | 1.67462 | 2.87504 |
| ---------- | | | | H | -3.81026 | 1.65875 | -0.87714 |
| | | | | C | -4.96868 | 1.88061 | 0.91710 |
| Compound **5.35** | | | | H | -4.76464 | 2.94881 | 1.05447 |
| This structure was assigned as correct. | | | | H | -5.09461 | 1.43194 | 1.90967 |
| B3LYP/6-31g(d) | | | | H | -5.91628 | 1.77874 | 0.38074 |
| SMD implicit solvation in dichloromethane was used. | | | | H | -4.30733 | -0.80185 | 0.84993 |
| | | | | O | -5.36533 | -0.32849 | -0.87333 |
| | | | | C | -6.17874 | -1.46591 | -0.63046 |
| Electronic Energy: -1232.73104646 hartree. | | | | H | -7.05463 | -1.37133 | -1.27932 |
| | | | | H | -6.51350 | -1.50578 | 0.41699 |
| Free Energy: -1232.289881 hartree. | | | | H | -5.66744 | -2.40996 | -0.86961 |
| | | | | H | 3.80996 | -1.65859 | -0.87755 |
| O | -2.03517 | -1.46158 | -0.00317 | C | 4.96883 | -1.88100 | 0.91633 |
| C | -0.92158 | -1.96596 | -0.56919 | H | 5.09528 | -1.43239 | 1.90886 |
| O | -0.77641 | -2.09081 | -1.76950 | H | 5.91624 | -1.77932 | 0.37959 |
| C | -3.08135 | -1.04042 | -0.90992 | H | 4.76460 | -2.94915 | 1.05374 |
| H | -3.50956 | -1.92982 | -1.38176 | H | 4.30706 | 0.80162 | 0.85014 |
| H | -2.65286 | -0.40944 | -1.69321 | O | 5.36541 | 0.32865 | -0.87298 |
| C | -4.15525 | -0.29099 | -0.11244 | C | 6.17842 | 1.46638 | -0.63027 |
| C | -3.83304 | 1.20718 | 0.12352 | H | 5.66699 | 2.41020 | -0.87000 |

| | | | |
|---|---|---|---|
| H | 7.05458 | 1.37176 | -1.27875 |
| H | 6.51278 | 1.50676 | 0.41729 |

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Compound **5.36**
This structure was assigned as ambiguous.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -64.906975 kJ.

| | | | |
|---|---|---|---|
| C | 3.80820 | 0.39840 | 20.13520 |
| H | 4.44560 | 0.52690 | 20.99790 |
| H | 2.79190 | 0.75600 | 20.21220 |
| C | 4.25130 | -0.19440 | 19.01290 |
| C | 5.62640 | -0.64830 | 18.91050 |
| H | 5.77350 | -1.61920 | 18.45880 |
| C | 6.69750 | 0.06180 | 19.32550 |
| H | 6.53170 | 1.03300 | 19.76900 |
| C | 8.16610 | -0.33960 | 19.20390 |
| H | 8.62720 | -0.36420 | 20.19180 |
| H | 8.67940 | 0.44060 | 18.64020 |
| C | 8.35220 | -1.67000 | 18.49300 |
| C | 8.31300 | -1.72900 | 17.14690 |
| H | 8.19640 | -0.80560 | 16.60420 |
| C | 8.42900 | -2.87800 | 19.41190 |
| H | 7.46530 | -3.04230 | 19.89460 |
| H | 9.17340 | -2.71040 | 20.19030 |
| H | 8.71130 | -3.79050 | 18.89180 |
| C | 8.19660 | -2.96850 | 16.28350 |
| H | 8.76430 | -3.79750 | 16.70360 |
| H | 8.64590 | -2.76930 | 15.31000 |
| C | 6.73100 | -3.34760 | 16.12730 |
| C | 4.09640 | -3.88940 | 16.04510 |
| C | 5.98370 | -2.70240 | 15.12000 |
| C | 6.23390 | -4.27170 | 17.06560 |
| C | 4.84400 | -4.54900 | 17.04620 |
| C | 4.61100 | -3.02550 | 15.05780 |
| H | 6.89430 | -4.71220 | 17.79430 |
| H | 3.97090 | -2.60190 | 14.30170 |
| O | 6.56360 | -1.83170 | 14.23420 |
| Si | 6.11820 | -0.23140 | 13.88180 |
| C | 7.19650 | 0.34620 | 12.41230 |
| C | 6.89980 | 1.82420 | 12.10310 |
| H | 7.50500 | 2.18460 | 11.27080 |
| H | 7.11230 | 2.46180 | 12.96200 |
| H | 5.85370 | 1.97460 | 11.83470 |
| C | 8.68110 | 0.17920 | 12.78130 |
| H | 9.33200 | 0.46720 | 11.95550 |
| H | 8.91080 | -0.85700 | 13.03470 |
| H | 8.95350 | 0.79230 | 13.64050 |
| C | 6.87140 | -0.51950 | 11.18300 |
| H | 7.48520 | -0.24280 | 10.32550 |
| H | 5.82740 | -0.41580 | 10.88540 |
| H | 7.04810 | -1.57680 | 11.38700 |
| C | 4.29040 | -0.12100 | 13.41030 |
| H | 4.04160 | -0.83100 | 12.62290 |
| H | 4.03420 | 0.87290 | 13.04780 |
| H | 3.64610 | -0.32820 | 14.26380 |
| C | 6.44260 | 0.88210 | 15.37100 |
| H | 5.97180 | 1.85570 | 15.24640 |
| H | 7.50620 | 1.05600 | 15.51930 |
| H | 6.05080 | 0.44230 | 16.28590 |
| C | 3.33310 | -0.34070 | 17.81290 |
| H | 3.94840 | -0.38370 | 16.91330 |
| H | 2.71330 | 0.55150 | 17.71450 |
| C | 2.45600 | -1.60020 | 17.88160 |
| H | 3.07160 | -2.46970 | 18.10800 |
| H | 1.74310 | -1.51200 | 18.70180 |
| C | 2.58340 | -4.11260 | 16.03390 |
| H | 2.23610 | -4.52250 | 16.98190 |
| H | 2.36550 | -4.87800 | 15.28850 |
| C | 1.73710 | -2.87080 | 15.76650 |
| C | 1.68230 | -1.80210 | 16.58870 |
| H | 1.03970 | -0.97660 | 16.31860 |
| C | 0.91390 | -2.92290 | 14.49350 |
| H | 0.34230 | -2.00660 | 14.34340 |
| H | 0.21260 | -3.75690 | 14.53060 |
| H | 1.56400 | -3.05970 | 13.62900 |
| O | 4.21410 | -5.39520 | 17.93430 |
| C | 4.98360 | -5.93850 | 18.99630 |
| H | 5.77520 | -6.58860 | 18.62170 |
| H | 5.42170 | -5.15270 | 19.61350 |
| H | 4.33870 | -6.53980 | 19.63670 |

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Compound **5.36**
This structure was assigned as unreactive.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1531.64333270 hartree.
Free Energy: -1531.067836 hartree.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| | | | | H | 3.09066 | -1.95490 | 1.86699 |
| C | -5.12045 | 2.20002 | -1.70567 | C | 3.53035 | -2.26741 | -1.45977 |
| H | -5.69818 | 2.84174 | -1.04422 | H | 4.52525 | -2.71332 | -1.57851 |
| H | -5.67575 | 1.61956 | -2.43793 | H | 3.17341 | -1.97305 | -2.45262 |
| C | -3.78351 | 2.13486 | -1.62816 | H | 2.86348 | -3.04918 | -1.07856 |
| C | -3.07098 | 2.95230 | -0.62889 | C | -2.98595 | 1.22170 | -2.53120 |
| H | -3.70430 | 3.52830 | 0.04853 | H | -2.16102 | 1.78559 | -2.98273 |
| C | -1.74107 | 3.03959 | -0.49763 | H | -3.62630 | 0.88240 | -3.35328 |
| H | -1.08987 | 2.46268 | -1.15456 | C | -2.40909 | -0.00429 | -1.79717 |
| C | -1.02412 | 3.80220 | 0.58778 | H | -1.63986 | -0.46836 | -2.42839 |
| H | -1.70225 | 4.52646 | 1.05405 | H | -1.88714 | 0.33429 | -0.89218 |
| H | -0.17745 | 4.34974 | 0.15852 | C | -1.85569 | -2.89809 | -0.92646 |
| C | -0.52916 | 2.79259 | 1.61195 | H | -1.96100 | -3.90919 | -0.51469 |
| C | 0.66397 | 2.20800 | 1.45493 | H | -1.39004 | -3.00579 | -1.91478 |
| H | 1.29407 | 2.54078 | 0.62958 | C | -3.24957 | -2.29239 | -1.07217 |
| C | -1.54521 | 2.40103 | 2.64821 | C | -3.46236 | -1.02343 | -1.44093 |
| H | -2.39860 | 1.90073 | 2.17079 | H | -4.49658 | -0.67688 | -1.49226 |
| H | -1.93970 | 3.29159 | 3.15238 | C | -4.38945 | -3.22303 | -0.76171 |
| H | -1.14250 | 1.72903 | 3.40905 | H | -5.35939 | -2.73312 | -0.88844 |
| C | 1.15080 | 0.97299 | 2.18528 | H | -4.31102 | -3.58460 | 0.27066 |
| H | 0.85764 | 0.98125 | 3.23936 | H | -4.36526 | -4.10711 | -1.41217 |
| H | 2.24336 | 0.92316 | 2.14293 | O | -2.44588 | -2.41080 | 1.70938 |
| C | 0.53084 | -0.22345 | 1.49169 | C | -2.94865 | -2.04814 | 2.98061 |
| C | -0.93844 | -2.07665 | -0.04986 | H | -3.21283 | -0.98449 | 3.01463 |
| C | 0.97773 | -0.60659 | 0.22514 | H | -3.84677 | -2.64829 | 3.13416 |
| C | -0.60877 | -0.84394 | 2.01555 | H | -2.22643 | -2.26924 | 3.77546 |
| C | -1.32695 | -1.77292 | 1.26516 | ---------- | | | |
| C | 0.24080 | -1.51973 | -0.53172 | | | | |
| H | -0.94199 | -0.56136 | 3.00853 | Compound **5.36** | | | |
| H | 0.56434 | -1.73798 | -1.54739 | This structure was assigned as ambiguous. | | | |
| O | 2.09854 | -0.01023 | -0.30364 | B3LYP/6-31g(d) | | | |
| Si | 3.59223 | -0.80872 | -0.28224 | SMD implicit solvation in dichloromethane | | | |
| C | 4.83080 | 0.50261 | -0.83985 | was used. | | | |
| C | 4.62361 | 1.78823 | -0.02866 | | | | |
| H | 5.35696 | 2.54961 | -0.33038 | Electronic Energy: -1532.24160425 har- | | | |
| H | 4.75371 | 1.61803 | 1.04759 | tree. | | | |
| H | 3.62312 | 2.20627 | -0.18591 | Free Energy: -1531.673941 hartree. | | | |
| C | 6.25568 | -0.01916 | -0.60741 | | | | |
| H | 6.99123 | 0.71517 | -0.96440 | C | -2.98496 | 2.74522 | -3.29394 |
| H | 6.44406 | -0.95741 | -1.14459 | H | -2.37726 | 3.58643 | -3.61905 |
| H | 6.45485 | -0.19506 | 0.45663 | H | -3.73506 | 2.38854 | -3.99651 |
| C | 4.63524 | 0.80542 | -2.33106 | C | -2.82025 | 2.16381 | -2.09298 |
| H | 5.32198 | 1.60183 | -2.65123 | C | -1.84594 | 2.63324 | -1.08455 |
| H | 3.61375 | 1.14190 | -2.54597 | H | -1.53167 | 1.88237 | -0.36090 |
| H | 4.83964 | -0.07440 | -2.95272 | C | -1.36432 | 3.88002 | -0.95432 |
| C | 3.95414 | -1.42029 | 1.45385 | H | -1.70013 | 4.65522 | -1.64465 |
| H | 4.20623 | -0.60635 | 2.14222 | C | -0.34504 | 4.33637 | 0.07557 |
| H | 4.79654 | -2.12189 | 1.44032 | H | -0.62902 | 5.34285 | 0.41617 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 0.62281 | 4.46000 | -0.43387 | C | -2.03150 | -3.04555 | -0.26903 |
| C | -0.19128 | 3.40685 | 1.26619 | H | -2.19591 | -3.86668 | 0.44104 |
| C | 0.77459 | 2.47428 | 1.26278 | H | -1.41251 | -3.47067 | -1.07108 |
| H | 1.44618 | 2.45048 | 0.40490 | C | -3.40085 | -2.67973 | -0.85282 |
| C | -1.23061 | 3.57565 | 2.34719 | C | -3.71462 | -1.59043 | -1.57491 |
| H | -2.23990 | 3.41223 | 1.94556 | H | -4.74365 | -1.53892 | -1.94001 |
| H | -1.21592 | 4.60246 | 2.73890 | C | -4.44906 | -3.74164 | -0.60623 |
| H | -1.09120 | 2.89348 | 3.18964 | H | -5.40122 | -3.50265 | -1.09175 |
| C | 0.96501 | 1.32733 | 2.23545 | H | -4.63265 | -3.86115 | 0.47085 |
| H | 0.54736 | 1.56140 | 3.21922 | H | -4.11784 | -4.72341 | -0.97522 |
| H | 2.03496 | 1.13465 | 2.37110 | O | -2.93644 | -1.75721 | 2.03500 |
| C | 0.27450 | 0.09015 | 1.67978 | C | -3.50591 | -1.10921 | 3.16618 |
| C | -1.22544 | -1.97008 | 0.43047 | H | -4.46045 | -1.60782 | 3.34860 |
| C | 0.81118 | -0.61721 | 0.59185 | H | -2.87031 | -1.21233 | 4.05528 |
| C | -0.98317 | -0.29246 | 2.17119 | H | -3.68788 | -0.04413 | 2.97273 |
| C | -1.72124 | -1.32032 | 1.57755 | ---------- | | | |
| C | 0.04831 | -1.61990 | -0.02217 | | | | |
| H | -1.38396 | 0.24257 | 3.02547 | Compound **5.36** | | | |
| H | 0.44069 | -2.12064 | -0.90241 | This structure was assigned as unreactive. | | | |
| O | 2.05065 | -0.25544 | 0.11994 | B3LYP/6-31g(d) | | | |
| Si | 3.31450 | -1.22377 | -0.48558 | SMD implicit solvation in dichloromethane | | | |
| C | 4.85116 | -0.08292 | -0.44899 | was used. | | | |
| C | 4.66678 | 1.08812 | -1.43755 | | | | |
| H | 5.54630 | 1.74909 | -1.41740 | Electronic Energy: -1532.24226611 har- | | | |
| H | 3.79212 | 1.70155 | -1.18932 | tree. | | | |
| H | 4.54678 | 0.73937 | -2.47076 | Free Energy: -1531.675534 hartree. | | | |
| C | 5.08017 | 0.48201 | 0.96766 | | | | |
| H | 5.97957 | 1.11564 | 0.98583 | C | 5.18253 | -0.90238 | -2.81406 |
| H | 5.22956 | -0.31345 | 1.70852 | H | 5.79702 | -1.79511 | -2.71579 |
| H | 4.23758 | 1.09685 | 1.30328 | H | 5.66928 | -0.01967 | -3.22267 |
| C | 6.09393 | -0.90179 | -0.86361 | C | 3.88613 | -0.89278 | -2.44751 |
| H | 6.98664 | -0.25924 | -0.87231 | C | 3.28366 | -2.12987 | -1.92419 |
| H | 5.99536 | -1.33035 | -1.86880 | H | 3.97598 | -2.96784 | -1.82276 |
| H | 6.29424 | -1.72541 | -0.16702 | C | 1.99454 | -2.32643 | -1.59793 |
| C | 3.51628 | -2.73361 | 0.62658 | H | 1.28243 | -1.50714 | -1.68595 |
| H | 3.82393 | -2.46099 | 1.64321 | C | 1.40720 | -3.60758 | -1.04797 |
| H | 4.26824 | -3.42267 | 0.22199 | H | 2.15087 | -4.41337 | -1.08513 |
| H | 2.57516 | -3.29102 | 0.70647 | H | 0.55703 | -3.91003 | -1.67466 |
| C | 2.93300 | -1.76511 | -2.25501 | C | 0.92823 | -3.36530 | 0.38223 |
| H | 3.84244 | -2.11232 | -2.76193 | C | -0.29687 | -2.85344 | 0.58440 |
| H | 2.51681 | -0.94200 | -2.84809 | H | -0.93636 | -2.72497 | -0.28862 |
| H | 2.21295 | -2.59170 | -2.28430 | C | 1.96894 | -3.57631 | 1.45142 |
| C | -3.62254 | 0.93134 | -1.70680 | H | 2.82324 | -2.90112 | 1.30222 |
| H | -4.56794 | 0.92218 | -2.26347 | H | 2.36785 | -4.59926 | 1.40392 |
| H | -3.88039 | 0.97808 | -0.64036 | H | 1.58367 | -3.41362 | 2.46114 |
| C | -2.87852 | -0.40271 | -1.97829 | C | -0.82448 | -2.19158 | 1.84590 |
| H | -2.67081 | -0.45103 | -3.05870 | H | -0.44445 | -2.67365 | 2.75210 |
| H | -1.90852 | -0.40327 | -1.47552 | H | -1.91750 | -2.25129 | 1.87088 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -0.35109 | -0.74505 | 1.80471 | C | 3.05570 | 0.42338 | 4.02322 |
| C | 0.96987 | 1.71465 | 1.29689 | H | 2.34445 | 0.21072 | 4.83164 |
| C | -0.86946 | 0.15902 | 0.86151 | H | 3.39092 | -0.52157 | 3.57665 |
| C | 0.75944 | -0.35066 | 2.56194 | H | 3.91853 | 0.95091 | 4.43623 |
| C | 1.40543 | 0.86910 | 2.33622 | ---------- | | | |
| C | -0.18930 | 1.35482 | 0.60505 | | | | |
| H | 1.14310 | -1.03966 | 3.30624 | Compound **5.36** | | | |
| H | -0.53523 | 1.99266 | -0.20196 | This structure was assigned as ambiguous. | | | |
| O | -1.98035 | -0.21541 | 0.14383 | B3LYP/6-31g(d) | | | |
| Si | -3.28444 | 0.71015 | -0.43644 | Gas phase. | | | |
| C | -4.71451 | -0.55020 | -0.62287 | | | | |
| C | -5.16535 | -1.05435 | 0.76415 | Electronic Energy: -1532.21609042 hartree. | | | |
| H | -5.96439 | -1.80362 | 0.66003 | | | | |
| H | -5.56135 | -0.24231 | 1.38688 | Free Energy: -1531.647661 hartree. | | | |
| H | -4.34396 | -1.52783 | 1.31579 | | | | |
| C | -5.91026 | 0.13519 | -1.32037 | C | 3.42380 | 1.59045 | 3.59934 |
| H | -6.75080 | -0.56817 | -1.41378 | H | 3.80778 | 2.60487 | 3.53629 |
| H | -5.65693 | 0.47343 | -2.33242 | H | 3.85516 | 0.95286 | 4.36741 |
| H | -6.27686 | 1.00395 | -0.75872 | C | 2.47375 | 1.13861 | 2.76527 |
| C | -4.26116 | -1.75282 | -1.47705 | C | 1.81968 | 1.98972 | 1.74943 |
| H | -5.09176 | -2.46234 | -1.60921 | H | 1.49169 | 1.48231 | 0.84244 |
| H | -3.43433 | -2.29852 | -1.00823 | C | 1.53127 | 3.29213 | 1.89212 |
| H | -3.93369 | -1.44619 | -2.47856 | H | 1.79423 | 3.78861 | 2.82727 |
| C | -3.69799 | 2.06276 | 0.81083 | C | 0.79086 | 4.16110 | 0.89005 |
| H | -3.80625 | 1.66057 | 1.82495 | H | 1.27842 | 5.14764 | 0.86306 |
| H | -4.64031 | 2.55884 | 0.54578 | H | -0.22082 | 4.34758 | 1.28151 |
| H | -2.92126 | 2.83559 | 0.84251 | C | 0.70493 | 3.58477 | -0.51079 |
| C | -2.83935 | 1.46923 | -2.10580 | C | -0.36721 | 2.86249 | -0.86988 |
| H | -3.68535 | 2.03578 | -2.51542 | H | -1.16449 | 2.74881 | -0.13675 |
| H | -2.56590 | 0.70298 | -2.84132 | C | 1.92000 | 3.81639 | -1.37487 |
| H | -1.99463 | 2.16372 | -2.02274 | H | 2.80482 | 3.33759 | -0.93448 |
| C | 3.07125 | 0.38699 | -2.56085 | H | 2.14537 | 4.88946 | -1.44479 |
| H | 2.01625 | 0.15755 | -2.74789 | H | 1.80175 | 3.43230 | -2.39078 |
| H | 3.42377 | 0.94949 | -3.43424 | C | -0.54552 | 2.02972 | -2.12607 |
| C | 3.17708 | 1.30937 | -1.32047 | H | -0.06092 | 2.49730 | -2.98977 |
| H | 2.85123 | 0.77004 | -0.42460 | H | -1.61255 | 1.94734 | -2.35942 |
| H | 4.24205 | 1.54528 | -1.16765 | C | 0.05455 | 0.65058 | -1.90080 |
| C | 1.77883 | 2.95011 | 0.92459 | C | 1.40200 | -1.73516 | -1.16223 |
| H | 2.80875 | 2.78699 | 1.25799 | C | -0.55427 | -0.27097 | -1.03370 |
| H | 1.41970 | 3.81262 | 1.50366 | C | 1.30054 | 0.32339 | -2.44789 |
| C | 1.76989 | 3.31486 | -0.55760 | C | 1.96623 | -0.85640 | -2.10509 |
| C | 2.39158 | 2.58769 | -1.50107 | C | 0.13246 | -1.43329 | -0.66678 |
| H | 2.34811 | 2.95757 | -2.52798 | H | 1.75980 | 1.02751 | -3.13261 |
| C | 1.03619 | 4.58617 | -0.91281 | H | -0.30297 | -2.09791 | 0.07135 |
| H | 1.05090 | 4.78213 | -1.99052 | O | -1.79184 | 0.04639 | -0.52999 |
| H | 1.47760 | 5.45529 | -0.40368 | Si | -3.00251 | -0.90092 | 0.18124 |
| H | -0.01362 | 4.54363 | -0.58793 | C | -4.53630 | 0.24377 | 0.19714 |
| O | 2.49714 | 1.29641 | 3.04854 | C | -4.25376 | 1.50536 | 1.04065 |

| | | | |
|---|---|---|---|
| H | -5.13260 | 2.16660 | 1.04355 |
| H | -3.41017 | 2.07881 | 0.64060 |
| H | -4.02778 | 1.26080 | 2.08556 |
| C | -4.89412 | 0.67260 | -1.24184 |
| H | -5.77190 | 1.33495 | -1.23554 |
| H | -5.13974 | -0.18727 | -1.87662 |
| H | -4.07072 | 1.21626 | -1.71789 |
| C | -5.73719 | -0.51159 | 0.80924 |
| H | -6.62535 | 0.13622 | 0.82423 |
| H | -5.54654 | -0.82236 | 1.84386 |
| H | -5.99994 | -1.40713 | 0.23259 |
| C | -3.30361 | -2.44912 | -0.85968 |
| H | -3.58234 | -2.19523 | -1.88857 |
| H | -4.11245 | -3.05450 | -0.43312 |
| H | -2.41038 | -3.08091 | -0.90956 |
| C | -2.50136 | -1.38338 | 1.93897 |
| H | -3.32926 | -1.87715 | 2.46248 |
| H | -2.21424 | -0.50314 | 2.52515 |
| H | -1.65065 | -2.07392 | 1.94881 |
| C | 2.01882 | -0.31253 | 2.80191 |
| H | 0.95006 | -0.36918 | 2.55923 |
| H | 2.13287 | -0.70615 | 3.81994 |
| C | 2.79758 | -1.23154 | 1.82601 |
| H | 2.79048 | -0.79835 | 0.82124 |
| H | 3.84955 | -1.24887 | 2.14964 |
| C | 2.17711 | -2.96010 | -0.69929 |
| H | 3.24245 | -2.76414 | -0.86041 |
| H | 1.94054 | -3.80366 | -1.36332 |
| C | 1.94846 | -3.39506 | 0.74625 |
| C | 2.24376 | -2.63310 | 1.81159 |
| H | 2.06688 | -3.06340 | 2.80009 |
| C | 1.40606 | -4.79427 | 0.92102 |
| H | 1.27122 | -5.05371 | 1.97610 |
| H | 2.07875 | -5.53941 | 0.47268 |
| H | 0.43747 | -4.91197 | 0.41375 |
| O | 3.19091 | -1.21841 | -2.61274 |
| C | 3.84995 | -0.32015 | -3.48655 |
| H | 4.04337 | 0.64775 | -3.00422 |
| H | 4.80122 | -0.79221 | -3.74090 |
| H | 3.27382 | -0.15239 | -4.40680 |

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Compound **5.36**
This structure was assigned as ambiguous.
M06-2X/6-31g(d)
SMD implicit solvation in dichloromethane was used.

Electronic Energy: -1531.64288520 hartree.
Free Energy: -1531.067520 hartree.

| | | | |
|---|---|---|---|
| C | -3.05435 | 2.09415 | -3.56261 |
| H | -3.33970 | 3.13689 | -3.44962 |
| H | -3.49386 | 1.55089 | -4.39611 |
| C | -2.21111 | 1.49517 | -2.71313 |
| C | -1.54716 | 2.20491 | -1.59796 |
| H | -1.28747 | 1.59284 | -0.73108 |
| C | -1.18750 | 3.49330 | -1.62173 |
| H | -1.39772 | 4.07853 | -2.51821 |
| C | -0.44239 | 4.23011 | -0.53086 |
| H | -0.93831 | 5.19634 | -0.36407 |
| H | 0.56189 | 4.46756 | -0.90813 |
| C | -0.34299 | 3.45825 | 0.76323 |
| C | 0.73757 | 2.71049 | 1.01257 |
| H | 1.54500 | 2.72270 | 0.28125 |
| C | -1.56402 | 3.49905 | 1.64298 |
| H | -2.39128 | 2.93990 | 1.18568 |
| H | -1.91040 | 4.53157 | 1.76959 |
| H | -1.38328 | 3.07703 | 2.63437 |
| C | 0.88018 | 1.71145 | 2.14171 |
| H | 0.52488 | 2.12604 | 3.09088 |
| H | 1.93726 | 1.45435 | 2.26974 |
| C | 0.06914 | 0.47607 | 1.80767 |
| C | -1.63289 | -1.60014 | 0.91482 |
| C | 0.42930 | -0.32403 | 0.72064 |
| C | -1.12332 | 0.18983 | 2.47830 |
| C | -1.96031 | -0.84085 | 2.05142 |
| C | -0.42300 | -1.33770 | 0.27955 |
| H | -1.39706 | 0.80421 | 3.32953 |
| H | -0.15152 | -1.89375 | -0.61346 |
| O | 1.59340 | -0.05157 | 0.04410 |
| Si | 2.94362 | -1.06686 | 0.16750 |
| C | 4.33324 | -0.06648 | -0.62779 |
| C | 3.95454 | 0.26926 | -2.07670 |
| H | 4.74958 | 0.86165 | -2.55134 |
| H | 3.02774 | 0.85280 | -2.12623 |
| H | 3.81493 | -0.63681 | -2.67913 |
| C | 4.54756 | 1.23472 | 0.15652 |
| H | 5.33983 | 1.83508 | -0.31272 |
| H | 4.85238 | 1.03982 | 1.19206 |
| H | 3.63772 | 1.84567 | 0.18126 |
| C | 5.63244 | -0.88314 | -0.61354 |
| H | 6.44955 | -0.30370 | -1.06559 |
| H | 5.53819 | -1.81529 | -1.18347 |
| H | 5.93961 | -1.14195 | 0.40733 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 3.27035 | -1.43591 | 1.97645 | H | 5.80180 | -2.63100 | -7.08130 |
| H | 3.45858 | -0.52844 | 2.56026 | H | 6.55670 | -1.06250 | -6.83700 |
| H | 4.14433 | -2.08971 | 2.08208 | O | 5.20670 | 1.94230 | -4.11440 |
| H | 2.41819 | -1.95562 | 2.42954 | H | 5.70880 | 2.08860 | -6.57730 |
| C | 2.62997 | -2.67204 | -0.75211 | C | 3.02900 | -2.04650 | -5.01890 |
| H | 3.54564 | -3.27341 | -0.79975 | H | 2.07900 | -1.52040 | -5.12670 |
| H | 2.28949 | -2.49499 | -1.77825 | C | 3.32120 | -1.74590 | -7.85940 |
| H | 1.86947 | -3.27583 | -0.24399 | O | 3.06830 | -1.42210 | -9.01840 |
| C | -1.91307 | 0.01363 | -2.81756 | O | 2.76300 | -2.84210 | -7.29350 |
| H | -0.90919 | -0.19024 | -2.42345 | C | 3.03070 | -3.26360 | -5.96280 |
| H | -1.91918 | -0.29434 | -3.86961 | H | 4.02890 | -3.70320 | -5.95980 |
| C | -2.93907 | -0.84027 | -2.04535 | C | 3.20460 | -2.43870 | -3.53720 |
| H | -3.01893 | -0.47506 | -1.01509 | H | 2.38450 | -3.05600 | -3.17290 |
| H | -3.92115 | -0.68761 | -2.51451 | H | 3.23990 | -1.55600 | -2.89770 |
| C | -2.62938 | -2.62592 | 0.40691 | H | 4.13030 | -2.99330 | -3.38040 |
| H | -3.62980 | -2.18685 | 0.49769 | C | 2.03190 | -4.39380 | -5.59870 |
| H | -2.63092 | -3.49098 | 1.08285 | H | 2.39220 | -4.89840 | -4.70200 |
| C | -2.39961 | -3.09807 | -1.01629 | H | 2.06720 | -5.15390 | -6.38030 |
| C | -2.56679 | -2.29659 | -2.07473 | C | 0.55910 | -3.98900 | -5.36020 |
| H | -2.38690 | -2.71328 | -3.06805 | H | 0.50270 | -3.29660 | -4.51960 |
| C | -1.95243 | -4.52635 | -1.16905 | O | -0.15470 | -5.16220 | -5.02760 |
| H | -1.78369 | -4.78971 | -2.21722 | Si | -1.28380 | -5.27500 | -3.77450 |
| H | -2.69297 | -5.22009 | -0.75173 | C | -2.03440 | -7.02790 | -3.82120 |
| H | -1.01861 | -4.69660 | -0.61633 | C | -2.72240 | -7.23720 | -5.18080 |
| O | -3.13960 | -1.16073 | 2.65694 | H | -3.53430 | -6.52510 | -5.33180 |
| C | -3.56335 | -0.34687 | 3.73403 | H | -3.14430 | -8.23900 | -5.26560 |
| H | -2.86063 | -0.39804 | 4.57400 | H | -2.01740 | -7.10540 | -6.00330 |
| H | -3.68189 | 0.69785 | 3.42125 | C | -0.90600 | -8.05870 | -3.64820 |
| H | -4.53012 | -0.74108 | 4.05011 | H | -0.40250 | -7.94330 | -2.68800 |
| ---------- | | | | H | -0.15040 | -7.94970 | -4.42790 |
| | | | | H | -1.28630 | -9.07920 | -3.69870 |
| Compound **5.37** | | | | C | -3.06110 | -7.17990 | -2.68570 |
| This structure was assigned as ambiguous. | | | | H | -3.87160 | -6.45660 | -2.78140 |
| | | | | H | -2.60090 | -7.02960 | -1.70860 |
| Molecular Mechanics (OPLS-2005), gas phase. | | | | H | -3.50890 | -8.17410 | -2.68680 |
| | | | | C | -2.61340 | -3.96450 | -4.03600 |
| Energy: -111.179916 kJ. | | | | H | -2.20420 | -2.95840 | -3.96720 |
| | | | | H | -3.40710 | -4.04870 | -3.29510 |
| C | 4.82840 | 1.17650 | -4.99100 | H | -3.07120 | -4.06410 | -5.01960 |
| C | 4.42830 | 0.56040 | -7.38600 | C | -0.37990 | -4.97500 | -2.14690 |
| C | 4.16540 | -1.10590 | -5.46160 | H | 0.04140 | -3.97250 | -2.09900 |
| C | 4.36900 | -0.96080 | -7.01050 | H | 0.43800 | -5.68240 | -2.01660 |
| O | 4.01150 | 0.12800 | -4.75700 | H | -1.04950 | -5.09030 | -1.29570 |
| N | 5.12320 | 1.30250 | -6.33680 | C | -0.06930 | -3.33250 | -6.57110 |
| H | 5.01590 | 0.67310 | -8.29670 | H | 0.02060 | -3.88740 | -7.49350 |
| H | 5.08530 | -1.53470 | -5.06140 | C | -0.64610 | -2.11820 | -6.55700 |
| C | 5.74670 | -1.57700 | -7.35520 | H | -0.69510 | -1.60460 | -5.60740 |
| H | 5.95650 | -1.51210 | -8.42420 | C | -1.12680 | -1.42130 | -7.73870 |

| | | | |
|---|---|---|---|
| C | -0.84390 | -1.98690 | -9.12570 |
| H | -1.50580 | -2.82910 | -9.32850 |
| H | 0.18620 | -2.34050 | -9.18960 |
| H | -0.96400 | -1.26450 | -9.92980 |
| C | -1.73700 | -0.23040 | -7.55800 |
| H | -1.87010 | 0.14340 | -6.55210 |
| C | -2.16200 | 0.75460 | -8.63800 |
| H | -3.12000 | 1.19380 | -8.35950 |
| H | -2.31010 | 0.27200 | -9.60160 |
| C | -1.11700 | 1.86690 | -8.77690 |
| O | -1.50190 | 3.03250 | -8.84750 |
| C | 0.30620 | 1.48740 | -8.80640 |
| H | 0.55080 | 0.43660 | -8.83740 |
| C | 1.30430 | 2.38680 | -8.75580 |
| H | 1.07180 | 3.44280 | -8.71610 |
| C | 2.68850 | 1.96720 | -8.66970 |
| C | 3.06460 | 1.21510 | -7.61340 |
| H | 2.32730 | 1.00160 | -6.85140 |
| C | 3.64010 | 2.30950 | -9.79880 |
| H | 3.16980 | 2.98870 | -10.51070 |
| H | 3.92980 | 1.40660 | -10.33780 |
| H | 4.53800 | 2.79420 | -9.41500 |

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Compound **5.37**

The reaction was unselective, so no "correct" or "incorrect" descriptor was assigned to this compound.

B3LYP/6-31g(d)

SMD implicit solvation in methanol was used.

Electronic Energy: -1926.64966603 hartree.

Free Energy: -1926.042654 hartree.

| | | | |
|---|---|---|---|
| C | -3.51868 | -3.86871 | -0.79323 |
| C | -3.40807 | -1.74023 | 0.59639 |
| C | -1.31205 | -3.10079 | -0.08113 |
| C | -1.97639 | -2.26141 | 1.02677 |
| O | -2.21036 | -4.12976 | -0.56037 |
| N | -4.03555 | -2.72876 | -0.28784 |
| H | -3.99503 | -1.71680 | 1.51700 |
| H | -0.50159 | -3.67926 | 0.37341 |
| C | -2.12469 | -3.12125 | 2.29943 |
| H | -2.56756 | -2.53734 | 3.10954 |
| H | -1.14775 | -3.48903 | 2.63092 |
| H | -2.76622 | -3.98552 | 2.10088 |
| O | -4.17481 | -4.68963 | -1.43080 |
| H | -5.02363 | -2.60188 | -0.47613 |
| C | -0.71320 | -2.29060 | -1.23822 |
| H | -1.49601 | -1.68344 | -1.70847 |
| C | -1.12519 | -1.03111 | 1.36281 |
| O | -1.28881 | -0.40409 | 2.39684 |
| O | -0.22167 | -0.57633 | 0.48834 |
| C | 0.33892 | -1.35504 | -0.62440 |
| H | 1.14067 | -1.95518 | -0.18103 |
| C | -0.09569 | -3.21596 | -2.29640 |
| H | 0.25570 | -2.65042 | -3.16405 |
| H | -0.83810 | -3.93675 | -2.65074 |
| H | 0.75298 | -3.77658 | -1.88504 |
| C | 0.93185 | -0.35744 | -1.61716 |
| H | 0.12379 | 0.20062 | -2.10401 |
| H | 1.43598 | -0.94473 | -2.39180 |
| C | 1.96672 | 0.66406 | -1.07796 |
| H | 2.38016 | 1.15166 | -1.97243 |
| O | 2.99914 | -0.05872 | -0.39555 |
| Si | 4.60149 | 0.46440 | -0.20870 |
| C | 5.47012 | -1.02084 | 0.62984 |
| C | 4.76972 | -1.35676 | 1.96341 |
| H | 4.79677 | -0.51528 | 2.66744 |
| H | 5.26664 | -2.20691 | 2.45481 |
| H | 3.71841 | -1.63204 | 1.81651 |
| C | 5.41856 | -2.25760 | -0.29092 |
| H | 5.90589 | -3.11751 | 0.19311 |
| H | 5.93761 | -2.08410 | -1.24200 |
| H | 4.38806 | -2.55337 | -0.52334 |
| C | 6.94535 | -0.66529 | 0.91287 |
| H | 7.04125 | 0.19488 | 1.58752 |
| H | 7.49936 | -0.43147 | -0.00541 |
| H | 7.45771 | -1.51276 | 1.39257 |
| C | 4.68004 | 2.01269 | 0.86763 |
| H | 4.24538 | 1.85329 | 1.86175 |
| H | 4.13915 | 2.84514 | 0.40109 |
| H | 5.71903 | 2.33899 | 1.00690 |
| C | 5.33390 | 0.86081 | -1.90277 |
| H | 4.82106 | 1.71036 | -2.37173 |
| H | 5.26812 | 0.01312 | -2.59557 |
| H | 6.39271 | 1.13679 | -1.81483 |
| C | 1.34645 | 1.72177 | -0.19762 |
| H | 1.26243 | 1.46925 | 0.85496 |
| C | 0.78637 | 2.84080 | -0.68932 |
| H | 0.87512 | 3.04195 | -1.75859 |
| C | -0.11265 | 3.73316 | 0.05197 |
| C | -0.22062 | 3.54508 | 1.54499 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.85277 | 4.30146 | 2.01563 | H | 0.39636 | -1.18304 | 0.90062 |
| H | 0.77137 | 3.60104 | 2.01112 | C | 1.76791 | -0.98967 | -1.66005 |
| H | -0.62908 | 2.55658 | 1.79319 | O | 2.31016 | -0.15023 | -2.36592 |
| C | -0.87997 | 4.58433 | -0.66843 | O | 0.43116 | -1.08023 | -1.70145 |
| H | -0.71860 | 4.62027 | -1.74598 | C | -0.29317 | -2.09095 | -0.90589 |
| C | -2.12491 | 5.31518 | -0.22045 | H | -0.18144 | -3.04290 | -1.43927 |
| H | -2.22828 | 6.27630 | -0.73452 | C | -0.41334 | -3.12942 | 1.42047 |
| H | -2.16205 | 5.47170 | 0.86092 | H | -1.39318 | -2.71979 | 1.68152 |
| C | -3.25546 | 4.38530 | -0.67499 | H | 0.14766 | -3.27322 | 2.34872 |
| O | -3.76109 | 4.50016 | -1.79157 | H | -0.56445 | -4.11402 | 0.96076 |
| C | -3.56599 | 3.25280 | 0.22697 | C | -1.76767 | -1.70010 | -0.97283 |
| H | -3.50429 | 3.43735 | 1.29618 | H | -2.35089 | -2.54441 | -0.58872 |
| C | -3.72366 | 2.00513 | -0.26289 | H | -2.03105 | -1.58918 | -2.03211 |
| H | -3.67487 | 1.86755 | -1.34281 | C | -2.23549 | -0.43285 | -0.23184 |
| C | -3.82393 | 0.78620 | 0.54612 | H | -2.05776 | -0.55358 | 0.84413 |
| C | -3.47519 | -0.37719 | -0.05271 | O | -3.66462 | -0.38846 | -0.47015 |
| H | -3.21181 | -0.35157 | -1.10874 | Si | -4.81698 | 0.49725 | 0.40311 |
| C | -4.22879 | 0.93912 | 1.99191 | C | -6.44370 | -0.46005 | 0.06950 |
| H | -5.12962 | 1.55950 | 2.06760 | C | -6.33469 | -1.90645 | 0.59405 |
| H | -3.44375 | 1.43941 | 2.57116 | H | -5.52712 | -2.46271 | 0.10294 |
| H | -4.43283 | -0.01594 | 2.47958 | H | -7.27184 | -2.45253 | 0.40499 |
| --- | | | | H | -6.15326 | -1.94096 | 1.67616 |
| | | | | C | -7.62139 | 0.24045 | 0.78341 |
| Compound **5.37** | | | | H | -7.48573 | 0.27680 | 1.87205 |
| This structure was assigned as ambiguous. | | | | H | -8.56003 | -0.30328 | 0.59452 |
| B3LYP/6-31g(d) | | | | H | -7.76817 | 1.26898 | 0.42944 |
| SMD implicit solvation in methanol was used. | | | | C | -6.73440 | -0.49273 | -1.44532 |
| | | | | H | -5.93958 | -0.99733 | -2.00802 |
| | | | | H | -6.85061 | 0.51550 | -1.86298 |
| Electronic Energy: -1926.65180521 hartree. | | | | H | -7.67150 | -1.03581 | -1.64342 |
| | | | | C | -4.94105 | 2.26959 | -0.23676 |
| Free Energy: -1926.042195 hartree. | | | | H | -4.01476 | 2.82539 | -0.04873 |
| | | | | H | -5.75276 | 2.81426 | 0.26421 |
| C | 3.79699 | -2.65958 | 1.68097 | H | -5.13520 | 2.30414 | -1.31629 |
| C | 3.93432 | -1.47154 | -0.46216 | C | -4.37069 | 0.52385 | 2.23583 |
| C | 1.80004 | -2.67765 | 0.30005 | H | -3.45281 | 1.09620 | 2.41946 |
| C | 2.56259 | -2.06273 | -0.92081 | H | -4.22411 | -0.48064 | 2.65065 |
| O | 2.45550 | -2.40905 | 1.58041 | H | -5.16721 | 1.00739 | 2.81699 |
| N | 4.48700 | -2.40362 | 0.54841 | C | -1.55469 | 0.81982 | -0.70939 |
| H | 4.61850 | -1.50923 | -1.31007 | H | -1.60803 | 1.00664 | -1.78094 |
| H | 1.80360 | -3.76635 | 0.18246 | C | -0.89836 | 1.66345 | 0.10703 |
| C | 2.82641 | -3.17785 | -1.97113 | H | -0.88634 | 1.44924 | 1.17763 |
| H | 3.30246 | -2.75662 | -2.86098 | C | -0.11526 | 2.83724 | -0.30576 |
| H | 1.89195 | -3.66400 | -2.26884 | C | -0.05476 | 3.13112 | -1.78321 |
| H | 3.48560 | -3.93699 | -1.53871 | H | -1.06618 | 3.21301 | -2.20347 |
| O | 4.25880 | -3.07921 | 2.73735 | H | 0.44376 | 2.31176 | -2.31903 |
| H | 5.49603 | -2.47716 | 0.61682 | H | 0.47654 | 4.05688 | -2.01493 |
| C | 0.35588 | -2.19472 | 0.47632 | C | 0.55250 | 3.52426 | 0.65135 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 0.42145 | 3.19179 | 1.68184 | H | -0.18220 | -3.18560 | -1.24635 |
| C | 1.55048 | 4.63199 | 0.47638 | C | -0.27956 | -3.04862 | 1.60762 |
| H | 1.36333 | 5.46338 | 1.16590 | H | -1.26542 | -2.65329 | 1.86826 |
| H | 1.53242 | 5.04320 | -0.54197 | H | 0.32223 | -3.09029 | 2.51919 |
| C | 2.99780 | 4.17502 | 0.71837 | H | -0.41322 | -4.07473 | 1.24187 |
| O | 3.80380 | 4.90702 | 1.29340 | C | -1.76762 | -1.83177 | -0.81755 |
| C | 3.35208 | 2.84286 | 0.19546 | H | -2.32546 | -2.66549 | -0.37679 |
| H | 2.58003 | 2.31284 | -0.35309 | H | -2.07989 | -1.77178 | -1.86644 |
| C | 4.54451 | 2.24424 | 0.38730 | C | -2.23882 | -0.53862 | -0.11702 |
| H | 5.35491 | 2.78125 | 0.88185 | H | -2.05220 | -0.61465 | 0.96473 |
| C | 4.81433 | 0.87237 | -0.08457 | O | -3.65147 | -0.51064 | -0.35040 |
| C | 3.84335 | -0.05243 | 0.04565 | Si | -4.81044 | 0.48877 | 0.36014 |
| H | 2.92681 | 0.22426 | 0.55945 | C | -6.45473 | -0.44646 | 0.06648 |
| C | 6.17234 | 0.62374 | -0.70756 | C | -6.66429 | -0.66796 | -1.44723 |
| H | 6.86625 | 1.43420 | -0.46459 | H | -6.72950 | 0.28023 | -1.99463 |
| H | 6.09661 | 0.58268 | -1.80245 | H | -7.60178 | -1.21419 | -1.62761 |
| H | 6.62293 | -0.31851 | -0.37498 | H | -5.84754 | -1.25208 | -1.88536 |
| ---------- | | | | C | -6.41226 | -1.82004 | 0.76984 |
| | | | | H | -6.30238 | -1.72174 | 1.85700 |
| Compound **5.37** | | | | H | -5.58289 | -2.43435 | 0.40170 |
| This structure was assigned as ambiguous. | | | | H | -7.34466 | -2.37385 | 0.58631 |
| B3LYP/6-31g(d) | | | | C | -7.63883 | 0.37095 | 0.62683 |
| Gas phase. | | | | H | -7.73107 | 1.35012 | 0.14131 |
| | | | | H | -7.55025 | 0.54004 | 1.70740 |
| Electronic Energy: -1926.60553141 hartree. | | | | H | -8.58462 | -0.16448 | 0.45992 |
| | | | | C | -4.83778 | 2.18933 | -0.46294 |
| Free Energy: -1925.997313 hartree. | | | | H | -3.88678 | 2.71071 | -0.31059 |
| | | | | H | -5.63324 | 2.82008 | -0.04701 |
| C | 3.90801 | -2.49272 | 1.67576 | H | -5.00419 | 2.11231 | -1.54352 |
| C | 3.94615 | -1.44999 | -0.54303 | C | -4.44130 | 0.69732 | 2.20440 |
| C | 1.87771 | -2.63481 | 0.37065 | H | -3.51529 | 1.26169 | 2.36621 |
| C | 2.57124 | -2.08254 | -0.92247 | H | -4.33935 | -0.26562 | 2.71790 |
| O | 2.55723 | -2.27638 | 1.59214 | H | -5.24602 | 1.25273 | 2.70126 |
| N | 4.54552 | -2.35805 | 0.46079 | C | -1.56331 | 0.70057 | -0.63833 |
| H | 4.58876 | -1.49312 | -1.42466 | H | -1.59465 | 0.82957 | -1.71734 |
| H | 1.89268 | -3.73143 | 0.31252 | C | -0.93262 | 1.59344 | 0.14490 |
| C | 2.82535 | -3.25884 | -1.90255 | H | -0.92934 | 1.42551 | 1.22387 |
| H | 3.23706 | -2.88711 | -2.84592 | C | -0.16940 | 2.76060 | -0.31216 |
| H | 1.90355 | -3.80576 | -2.12724 | C | -0.08214 | 2.99161 | -1.80224 |
| H | 3.53847 | -3.95778 | -1.45430 | H | 0.44020 | 2.15920 | -2.29203 |
| O | 4.44018 | -2.76242 | 2.72570 | H | 0.44378 | 3.91463 | -2.05428 |
| H | 5.55236 | -2.31340 | 0.56438 | H | -1.08364 | 3.05021 | -2.24574 |
| C | 0.42520 | -2.17578 | 0.56031 | C | 0.47143 | 3.50932 | 0.61485 |
| H | 0.45475 | -1.13669 | 0.91349 | H | 0.34070 | 3.22697 | 1.66039 |
| C | 1.71473 | -1.08059 | -1.70652 | C | 1.44921 | 4.62995 | 0.39390 |
| O | 2.19684 | -0.21019 | -2.39762 | H | 1.25351 | 5.47472 | 1.06257 |
| O | 0.37547 | -1.24762 | -1.70157 | H | 1.40279 | 5.01079 | -0.63442 |
| C | -0.27772 | -2.18432 | -0.80037 | C | 2.91037 | 4.19526 | 0.65084 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O | 3.68107 | 4.90968 | 1.27311 | H | 0.98985 | -3.80200 | -0.86006 |
| C | 3.29400 | 2.87527 | 0.09828 | C | 1.92305 | -1.53171 | 1.28868 |
| H | 2.55939 | 2.35438 | -0.50652 | H | 2.58811 | -2.31462 | 0.90663 |
| C | 4.48185 | 2.28814 | 0.33565 | H | 2.13133 | -1.43314 | 2.36081 |
| H | 5.24127 | 2.84455 | 0.88642 | C | 2.30074 | -0.20776 | 0.61279 |
| C | 4.80011 | 0.93034 | -0.13781 | H | 2.24701 | -0.31400 | -0.48102 |
| C | 3.84949 | -0.02097 | -0.05278 | O | 3.64802 | 0.05270 | 1.01907 |
| H | 2.92110 | 0.24707 | 0.44407 | Si | 4.82214 | 0.75047 | 0.02838 |
| C | 6.19515 | 0.72382 | -0.68082 | C | 5.69942 | -0.62948 | -0.93282 |
| H | 6.94270 | 0.97943 | 0.08167 | C | 6.51896 | -1.48384 | 0.04270 |
| H | 6.38202 | 1.38028 | -1.53952 | H | 7.31404 | -0.90172 | 0.52379 |
| H | 6.38357 | -0.30508 | -0.99938 | H | 6.99710 | -2.32055 | -0.48662 |
| --- | | | | H | 5.88922 | -1.91120 | 0.83353 |
| | | | | C | 4.66411 | -1.52137 | -1.62975 |
| Compound **5.37** | | | | H | 4.03195 | -0.95413 | -2.32535 |
| This structure was assigned as ambiguous. | | | | H | 4.00933 | -2.01644 | -0.90158 |
| M06-2X/6-31g(d) | | | | H | 5.16467 | -2.31031 | -2.20964 |
| SMD implicit solvation in methanol was used. | | | | C | 6.63257 | -0.01813 | -1.98562 |
| | | | | H | 7.37264 | 0.65779 | -1.53825 |
| | | | | H | 6.07640 | 0.54752 | -2.74272 |
| Electronic Energy: -1925.92823689 hartree. | | | | H | 7.18730 | -0.81020 | -2.50876 |
| | | | | C | 6.00064 | 1.59646 | 1.20939 |
| Free Energy: -1925.312116 hartree. | | | | H | 5.53178 | 2.48022 | 1.65692 |
| | | | | H | 6.91125 | 1.92768 | 0.69645 |
| C | -3.37683 | -2.57957 | -1.70724 | H | 6.30042 | 0.92910 | 2.02492 |
| C | -3.68825 | -1.60529 | 0.48078 | C | 4.06803 | 2.00250 | -1.14750 |
| C | -1.47862 | -2.59217 | -0.24682 | H | 3.50450 | 2.76832 | -0.60355 |
| C | -2.32865 | -2.14498 | 0.97626 | H | 3.39834 | 1.55211 | -1.88883 |
| O | -2.07982 | -2.23905 | -1.51101 | H | 4.87137 | 2.51174 | -1.69393 |
| N | -4.13173 | -2.52087 | -0.58209 | C | 1.42286 | 0.93749 | 1.03307 |
| H | -4.41440 | -1.68923 | 1.29309 | H | 1.32270 | 1.08072 | 2.10855 |
| H | -1.40992 | -3.68717 | -0.23035 | C | 0.79450 | 1.73955 | 0.16421 |
| C | -2.57152 | -3.35248 | 1.90392 | H | 0.93447 | 1.56696 | -0.90488 |
| H | -3.12014 | -3.03910 | 2.79680 | C | -0.12066 | 2.83335 | 0.52550 |
| H | -1.63002 | -3.81426 | 2.21671 | C | -0.42348 | 3.01357 | 1.98803 |
| H | -3.16107 | -4.10200 | 1.36766 | H | -0.86834 | 2.09767 | 2.39761 |
| O | -3.76803 | -2.89203 | -2.81573 | H | -1.11002 | 3.83940 | 2.17998 |
| H | -5.13080 | -2.60871 | -0.74001 | H | 0.49745 | 3.20139 | 2.55221 |
| C | -0.07236 | -2.00397 | -0.27919 | C | -0.67243 | 3.55615 | -0.46692 |
| H | -0.15719 | -0.95742 | -0.60602 | H | -0.38876 | 3.30952 | -1.49025 |
| C | -1.64601 | -1.10523 | 1.85248 | C | -1.72878 | 4.61979 | -0.34403 |
| O | -2.27297 | -0.29675 | 2.50774 | H | -1.50594 | 5.48269 | -0.97845 |
| O | -0.32172 | -1.14976 | 1.98510 | H | -1.83136 | 4.97555 | 0.68786 |
| C | 0.48611 | -2.01107 | 1.13857 | C | -3.08741 | 4.07307 | -0.76574 |
| H | 0.42273 | -3.02558 | 1.55279 | O | -3.81546 | 4.68215 | -1.53602 |
| C | 0.80820 | -2.79172 | -1.24506 | C | -3.44440 | 2.75211 | -0.20375 |
| H | 1.77484 | -2.30578 | -1.40245 | H | -2.83336 | 2.37413 | 0.61266 |
| H | 0.31260 | -2.88121 | -2.21587 | C | -4.42263 | 1.99180 | -0.71596 |

| | | | |
|---|---|---|---|
| H | -5.06041 | 2.39406 | -1.50487 |
| C | -4.66897 | 0.61224 | -0.26126 |
| C | -3.61176 | -0.17334 | -0.00568 |
| H | -2.61661 | 0.22761 | -0.19451 |
| C | -6.10749 | 0.17873 | -0.16611 |
| H | -6.53443 | 0.06504 | -1.17014 |
| H | -6.70487 | 0.93412 | 0.35482 |
| H | -6.22551 | -0.77133 | 0.36071 |

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Compound **5.38**
This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.
Energy: -52.962257 kJ.

| | | | |
|---|---|---|---|
| N | -7.63130 | -0.88060 | -2.28970 |
| C | -6.41860 | -0.33370 | -2.34850 |
| O | -5.85040 | -0.40280 | -3.58440 |
| C | -6.75280 | -1.11500 | -4.32860 |
| C | -7.82150 | -1.45290 | -3.53980 |
| C | -9.00580 | -2.33020 | -3.84360 |
| H | -6.49680 | -1.33400 | -5.35560 |
| C | -8.92500 | -3.63770 | -3.02180 |
| O | -9.05970 | -2.62560 | -5.23730 |
| H | -9.91040 | -1.78870 | -3.56180 |
| C | -10.33030 | -3.04880 | -5.70760 |
| H | -10.64430 | -3.98900 | -5.25530 |
| H | -10.28010 | -3.20460 | -6.78520 |
| H | -11.09460 | -2.29440 | -5.51730 |
| H | -9.78070 | -4.28510 | -3.20410 |
| H | -8.96260 | -3.38570 | -1.96100 |
| C | -7.64770 | -4.41150 | -3.29100 |
| C | -6.58420 | -4.41420 | -2.47020 |
| H | -7.59660 | -4.91960 | -4.24340 |
| H | -6.63960 | -3.85490 | -1.54520 |
| C | -5.34360 | -5.07550 | -2.80470 |
| C | -4.23450 | -4.96480 | -2.05800 |
| H | -5.29420 | -5.65940 | -3.71230 |
| H | -4.25070 | -4.37630 | -1.15100 |
| C | -2.89890 | -5.58140 | -2.43070 |
| C | -1.78970 | -4.52120 | -2.54350 |
| H | -2.98770 | -6.08610 | -3.39490 |
| O | -2.47840 | -6.52160 | -1.45060 |
| C | -3.25050 | -7.71330 | -1.41720 |
| H | -3.23220 | -8.22320 | -2.38110 |
| H | -4.28820 | -7.51720 | -1.14520 |
| H | -2.83660 | -8.39270 | -0.67230 |
| C | -2.04730 | -3.40090 | -3.57620 |
| H | -0.85550 | -5.02580 | -2.79150 |
| H | -1.63610 | -4.07350 | -1.56070 |
| C | -0.87010 | -2.39770 | -3.63160 |
| H | -2.97650 | -2.88930 | -3.31700 |
| O | -2.20600 | -3.95820 | -4.87320 |
| Si | -3.13050 | -3.26060 | -6.11350 |
| C | -2.29660 | -3.71560 | -7.76790 |
| C | -4.88040 | -3.95130 | -6.06350 |
| C | -3.19010 | -1.38420 | -5.91020 |
| C | -0.84970 | -3.19310 | -7.75520 |
| C | -3.07340 | -3.07560 | -8.93120 |
| C | -2.29180 | -5.24620 | -7.91900 |
| H | -1.77100 | -5.72210 | -7.08640 |
| H | -1.79490 | -5.55590 | -8.83870 |
| H | -3.30480 | -5.64900 | -7.94130 |
| H | -3.09600 | -1.98870 | -8.84470 |
| H | -4.10580 | -3.42530 | -8.96120 |
| H | -2.61850 | -3.31780 | -9.89210 |
| H | -0.81600 | -2.10760 | -7.65940 |
| H | -0.32170 | -3.45800 | -8.67160 |
| H | -0.28760 | -3.61200 | -6.91880 |
| H | -5.47050 | -3.60970 | -6.91230 |
| H | -4.87820 | -5.03980 | -6.07820 |
| H | -5.39990 | -3.63010 | -5.16290 |
| H | -3.84650 | -0.94030 | -6.65430 |
| H | -2.21010 | -0.92780 | -6.03180 |
| H | -3.57560 | -1.10080 | -4.93170 |
| C | -0.92740 | -1.29240 | -2.57860 |
| H | -0.84420 | -1.90090 | -4.59840 |
| H | 0.07940 | -2.92600 | -3.54610 |
| O | 0.04870 | -1.01390 | -1.88470 |
| O | -2.11420 | -0.65690 | -2.56020 |
| C | -2.33930 | 0.50200 | -1.75940 |
| C | -3.15470 | 0.14290 | -0.46630 |
| C | -2.96950 | 1.54710 | -2.71060 |
| H | -1.38420 | 0.91450 | -1.43060 |
| C | -2.01590 | 2.06090 | -3.81030 |
| H | -3.84590 | 1.10160 | -3.16760 |
| H | -3.32220 | 2.41470 | -2.15580 |
| O | -1.04640 | 2.84920 | -3.12830 |
| C | -2.73890 | 2.95360 | -4.85250 |
| H | -1.55710 | 1.21630 | -4.32890 |
| C | 0.29730 | 2.44900 | -3.35740 |
| H | 0.55280 | 2.49690 | -4.41630 |
| H | 0.47440 | 1.43380 | -3.00300 |
| H | 0.97340 | 3.11270 | -2.81870 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.75000 | 3.73290 | -5.73790 | H | -8.84800 | 3.66970 | -7.80000 |
| H | -3.31840 | 3.68900 | -4.29750 | C | -6.20610 | 5.81860 | -7.09400 |
| C | -3.69980 | 2.14890 | -5.75470 | H | -5.11680 | 5.75490 | -7.07980 |
| H | -1.09970 | 3.05930 | -6.29570 | H | -6.53430 | 6.09720 | -6.09290 |
| H | -1.11960 | 4.39560 | -5.14500 | H | -6.47940 | 6.63610 | -7.76160 |
| H | -2.27810 | 4.35690 | -6.45960 | C | -6.42120 | 4.20210 | -8.99990 |
| H | -3.13130 | 1.51560 | -6.43570 | H | -6.85500 | 3.26910 | -9.36210 |
| O | -4.51180 | 3.02700 | -6.51520 | H | -6.74310 | 4.99660 | -9.67360 |
| H | -4.34130 | 1.47890 | -5.18430 | H | -5.33760 | 4.11170 | -9.08910 |
| Si | -6.20620 | 3.05850 | -6.43200 | C | -6.83630 | 4.48900 | -7.54560 |
| C | -6.75770 | 1.38130 | -7.12170 | | | | |
| C | -6.57560 | 3.33430 | -4.59000 | ---------- | | | |
| C | -7.12860 | 3.81880 | -1.84890 | | | | |
| C | -5.93840 | 4.38680 | -3.89840 | Compound **5.38** | | | |
| C | -7.49480 | 2.52740 | -3.88510 | This structure was assigned as incorrect. | | | |
| C | -7.77610 | 2.76950 | -2.52630 | | | | |
| C | -6.20510 | 4.62730 | -2.53640 | Molecular Mechanics (OPLS-2005), gas | | | |
| H | -5.23380 | 5.01620 | -4.42350 | phase. | | | |
| H | -7.98640 | 1.70200 | -4.37620 | Energy: -52.562019 kJ. | | | |
| H | -8.48380 | 2.13940 | -2.00520 | | | | |
| H | -5.70770 | 5.43850 | -2.02410 | N | -7.21680 | -2.72940 | 0.50430 |
| H | -7.34410 | 4.00640 | -0.80680 | C | -7.37600 | -1.69200 | -0.31740 |
| C | -7.57150 | -1.12040 | -8.17870 | O | -7.95050 | -2.02490 | -1.50520 |
| C | -5.85660 | 0.58120 | -7.85710 | C | -8.13320 | -3.37780 | -1.42550 |
| C | -8.08520 | 0.92890 | -6.96110 | C | -7.69650 | -3.82250 | -0.20490 |
| C | -8.48960 | -0.31690 | -7.47810 | C | -7.66160 | -5.22590 | 0.34350 |
| C | -6.25520 | -0.66590 | -8.37710 | H | -8.56330 | -3.87400 | -2.28310 |
| H | -4.84880 | 0.93120 | -8.02690 | C | -6.27080 | -5.86680 | 0.19530 |
| H | -8.80360 | 1.54130 | -6.43620 | O | -8.59870 | -6.07980 | -0.30460 |
| H | -9.50390 | -0.65880 | -7.33280 | H | -7.89200 | -5.20470 | 1.41030 |
| H | -5.55300 | -1.27070 | -8.93210 | C | -9.94470 | -5.86440 | 0.09580 |
| H | -7.88090 | -2.07870 | -8.57040 | H | -10.07410 | -6.05470 | 1.16200 |
| C | -4.52200 | -0.52280 | -0.79080 | H | -10.59850 | -6.54820 | -0.44550 |
| C | -3.37630 | 1.40270 | 0.40740 | H | -10.27640 | -4.84800 | -0.11840 |
| C | -2.31280 | -0.82550 | 0.40600 | H | -6.29450 | -6.89150 | 0.56600 |
| H | -2.42400 | 1.86800 | 0.66530 | H | -5.55950 | -5.32480 | 0.81980 |
| H | -3.87470 | 1.15200 | 1.34520 | C | -5.77200 | -5.87470 | -1.23760 |
| H | -3.98050 | 2.16990 | -0.07380 | C | -4.63070 | -5.29700 | -1.64460 |
| H | -2.80090 | -1.03750 | 1.35820 | H | -6.41480 | -6.36880 | -1.95290 |
| H | -1.32900 | -0.41040 | 0.62760 | H | -4.01120 | -4.80100 | -0.91040 |
| H | -2.15120 | -1.78840 | -0.07990 | C | -4.21360 | -5.27970 | -3.02880 |
| O | -4.67680 | -1.73640 | -0.63300 | C | -3.06250 | -4.71930 | -3.43150 |
| C | -5.69360 | 0.36000 | -1.24500 | H | -4.86320 | -5.71720 | -3.77280 |
| H | -5.36890 | 1.33810 | -1.58950 | H | -2.39750 | -4.27370 | -2.70560 |
| H | -6.37590 | 0.50960 | -0.40960 | C | -2.60670 | -4.63250 | -4.87790 |
| C | -8.36910 | 4.58490 | -7.45080 | C | -2.37530 | -3.17210 | -5.29890 |
| H | -8.69310 | 4.75350 | -6.42290 | H | -3.36350 | -5.06630 | -5.53380 |
| H | -8.75460 | 5.40570 | -8.05630 | O | -1.37790 | -5.32290 | -5.06010 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -1.49180 | -6.73730 | -4.99910 | H | -0.53000 | 1.46840 | -1.94590 |
| H | -2.18010 | -7.11110 | -5.75820 | H | 0.03420 | 2.99090 | -2.65080 |
| H | -1.83410 | -7.07510 | -4.02040 | H | 0.22200 | 2.68920 | -0.92380 |
| H | -0.51650 | -7.18810 | -5.18220 | C | -1.67430 | 5.24610 | -3.46310 |
| C | -3.64450 | -2.29250 | -5.26340 | H | -3.42460 | 5.02080 | -2.26340 |
| H | -1.95650 | -3.14810 | -6.30560 | C | -3.92810 | 4.49730 | -4.28300 |
| H | -1.60840 | -2.74740 | -4.65040 | H | -1.13480 | 4.73770 | -4.26290 |
| C | -3.32340 | -0.79120 | -5.41230 | H | -1.00020 | 5.34120 | -2.61200 |
| H | -4.15340 | -2.44440 | -4.31150 | H | -1.90330 | 6.25490 | -3.80620 |
| O | -4.51910 | -2.72300 | -6.29650 | H | -4.93000 | 4.18210 | -3.99550 |
| Si | -6.16990 | -2.35580 | -6.37950 | O | -3.41950 | 3.65390 | -5.29970 |
| C | -7.08510 | -3.92600 | -6.96500 | H | -4.03060 | 5.51450 | -4.65590 |
| C | -6.78520 | -1.84400 | -4.67020 | Si | -4.06360 | 3.44480 | -6.85380 |
| C | -6.40250 | -0.97200 | -7.63600 | C | -2.97900 | 2.07640 | -7.55800 |
| C | -6.55850 | -4.32380 | -8.35420 | C | -5.84380 | 2.84500 | -6.60880 |
| C | -8.59520 | -3.64200 | -7.03780 | C | -8.47830 | 1.86040 | -6.24010 |
| C | -6.81550 | -5.06440 | -5.96730 | C | -6.18730 | 2.11780 | -5.44920 |
| H | -7.15300 | -4.80740 | -4.96280 | C | -6.83320 | 3.04260 | -7.59700 |
| H | -5.74960 | -5.28460 | -5.90990 | C | -8.14400 | 2.55990 | -7.41410 |
| H | -7.32450 | -5.98250 | -6.26150 | C | -7.49690 | 1.63730 | -5.25770 |
| H | -8.81460 | -2.83030 | -7.73230 | H | -5.43600 | 1.91920 | -4.69980 |
| H | -8.99440 | -3.35610 | -6.06410 | H | -6.59190 | 3.56940 | -8.50660 |
| H | -9.14850 | -4.51910 | -7.37420 | H | -8.89260 | 2.72430 | -8.17570 |
| H | -6.75040 | -3.54480 | -9.09250 | H | -7.74390 | 1.08990 | -4.35910 |
| H | -7.02910 | -5.23920 | -8.71350 | H | -9.48210 | 1.48820 | -6.09550 |
| H | -5.48060 | -4.49270 | -8.33290 | C | -1.32960 | 0.04230 | -8.62710 |
| H | -6.62470 | -2.63080 | -3.93500 | C | -1.64340 | 1.93760 | -7.12560 |
| H | -7.85010 | -1.61800 | -4.67860 | C | -3.47720 | 1.19450 | -8.54000 |
| H | -6.27210 | -0.95360 | -4.30930 | C | -2.65960 | 0.17680 | -9.06910 |
| H | -7.45460 | -0.72880 | -7.77440 | C | -0.82020 | 0.92490 | -7.65560 |
| H | -5.99150 | -1.24480 | -8.60630 | H | -1.25470 | 2.60920 | -6.37240 |
| H | -5.90210 | -0.06110 | -7.31550 | H | -4.49770 | 1.29380 | -8.88180 |
| C | -2.84430 | -0.17260 | -4.10200 | H | -3.05330 | -0.50230 | -9.81160 |
| H | -4.20740 | -0.23730 | -5.72340 | H | 0.19810 | 0.82070 | -7.30960 |
| H | -2.57370 | -0.63740 | -6.18610 | H | -0.70200 | -0.73990 | -9.02910 |
| O | -1.64900 | -0.09490 | -3.82130 | C | -6.05930 | 0.22570 | -1.11820 |
| O | -3.86960 | 0.21650 | -3.31990 | C | -4.06540 | 0.34550 | 0.45420 |
| C | -3.65800 | 0.73940 | -2.00590 | C | -4.25980 | -1.56470 | -1.15340 |
| C | -4.53280 | -0.05160 | -0.96790 | H | -2.97680 | 0.35670 | 0.52280 |
| C | -3.84850 | 2.27960 | -2.03830 | H | -4.41510 | -0.35430 | 1.21390 |
| H | -2.62370 | 0.55750 | -1.71330 | H | -4.41470 | 1.33740 | 0.74290 |
| C | -2.62810 | 3.04460 | -2.58920 | H | -4.61000 | -2.15760 | -0.30850 |
| H | -4.73110 | 2.50350 | -2.62890 | H | -3.19310 | -1.76510 | -1.25930 |
| H | -4.06550 | 2.66940 | -1.04550 | H | -4.75220 | -1.95710 | -2.04450 |
| O | -1.70320 | 3.13290 | -1.50820 | O | -6.51450 | 0.85880 | -2.07040 |
| C | -2.95370 | 4.47830 | -3.08430 | C | -7.02710 | -0.27010 | -0.03800 |
| H | -2.20080 | 2.49380 | -3.42770 | H | -7.93700 | 0.32810 | -0.06230 |
| C | -0.43950 | 2.54140 | -1.77720 | H | -6.59950 | -0.18470 | 0.95840 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.48540 | 5.68360 | -7.53930 | H | -3.34801 | 2.99220 | 2.78780 |
| H | -1.67750 | 4.99010 | -7.77730 | H | -4.88850 | 1.58731 | 0.53448 |
| H | -2.30750 | 6.60050 | -8.10180 | C | -4.62424 | 0.57308 | 2.48445 |
| H | -2.39810 | 5.92680 | -6.48010 | C | -3.60353 | -0.55681 | 2.25149 |
| C | -3.91350 | 4.76050 | -9.37570 | H | -5.63603 | 0.15774 | 2.36456 |
| H | -4.86010 | 4.30990 | -9.66920 | O | -4.44836 | 0.96766 | 3.85054 |
| H | -3.12260 | 4.06660 | -9.66450 | C | -5.58914 | 1.60717 | 4.41129 |
| H | -3.78430 | 5.66320 | -9.97360 | H | -6.45526 | 0.92901 | 4.43014 |
| C | -4.96610 | 6.08940 | -7.51740 | H | -5.86656 | 2.51651 | 3.86190 |
| H | -4.96020 | 6.35480 | -6.46220 | H | -5.32868 | 1.87866 | 5.43865 |
| H | -4.84310 | 7.01490 | -8.08070 | C | -3.64506 | -1.22049 | 0.87279 |
| H | -5.95910 | 5.70480 | -7.74620 | H | -3.78121 | -1.33094 | 3.00952 |
| C | -3.86100 | 5.07350 | -7.86780 | H | -2.59706 | -0.15576 | 2.41774 |
| | | | | C | -2.54669 | -2.31336 | 0.75223 |
| ---------- | | | | H | -3.48061 | -0.46796 | 0.09058 |
| | | | | O | -4.93051 | -1.82503 | 0.69655 |
| Compound **5.38** | | | | Si | -5.75148 | -2.03274 | -0.77545 |
| This structure was assigned as incorrect. | | | | C | -7.50756 | -2.58251 | -0.24584 |
| B3LYP/6-31g(d) | | | | C | -5.76553 | -0.41016 | -1.73973 |
| SMD implicit solvation in methanol was used. | | | | C | -4.91666 | -3.35228 | -1.83829 |
| | | | | C | -7.42065 | -3.82994 | 0.65914 |
| Electronic Energy: -3261.36754630 hartree. | | | | C | -8.33760 | -2.92854 | -1.50105 |
| Free Energy: -3260.304082 hartree. | | | | C | -8.21440 | -1.44884 | 0.52573 |
| | | | | H | -7.66793 | -1.16651 | 1.43416 |
| | | | | H | -9.22154 | -1.76537 | 0.83649 |
| | | | | H | -8.33150 | -0.54610 | -0.08682 |
| N | -0.22603 | 3.70113 | -0.54165 | H | -7.90015 | -3.75899 | -2.06890 |
| C | -0.02238 | 2.86510 | -1.51496 | H | -8.43469 | -2.07286 | -2.18163 |
| O | -0.27526 | 3.39263 | -2.74524 | H | -9.35576 | -3.23194 | -1.21462 |
| C | -0.68551 | 4.68278 | -2.49889 | H | -6.94298 | -4.67606 | 0.14892 |
| C | -0.65771 | 4.87930 | -1.15723 | H | -8.42769 | -4.15703 | 0.95915 |
| C | -1.04012 | 6.11104 | -0.37869 | H | -6.85310 | -3.63179 | 1.57625 |
| H | -0.94004 | 5.28252 | -3.35858 | H | -6.29156 | -0.54064 | -2.69468 |
| C | -2.51889 | 6.09373 | 0.07491 | H | -4.74764 | -0.07537 | -1.97930 |
| O | -0.88114 | 7.28701 | -1.17424 | H | -6.26668 | 0.39980 | -1.19677 |
| H | -0.39656 | 6.17544 | 0.51177 | H | -3.89387 | -3.06324 | -2.11081 |
| C | 0.47336 | 7.69706 | -1.33742 | H | -5.46930 | -3.49073 | -2.77674 |
| H | 0.94627 | 7.89957 | -0.36550 | H | -4.86539 | -4.32647 | -1.33738 |
| H | 0.45446 | 8.61957 | -1.92477 | C | -1.19863 | -1.75029 | 0.36805 |
| H | 1.07017 | 6.94622 | -1.87195 | H | -2.84850 | -3.04426 | 0.00212 |
| H | -3.15262 | 5.98652 | -0.81359 | H | -2.43559 | -2.83174 | 1.71138 |
| H | -2.71982 | 7.08062 | 0.51429 | O | -0.50667 | -1.04031 | 1.08267 |
| C | -2.81248 | 5.01417 | 1.07421 | O | -0.86142 | -2.11903 | -0.88004 |
| C | -3.57364 | 3.93136 | 0.83671 | C | 0.45177 | -1.78099 | -1.42277 |
| H | -2.33423 | 5.11855 | 2.04982 | C | 0.21294 | -0.86863 | -2.67450 |
| H | -4.04303 | 3.81358 | -0.14161 | C | 1.17957 | -3.09603 | -1.72340 |
| C | -3.78421 | 2.85944 | 1.79748 | H | 0.99322 | -1.21438 | -0.66369 |
| C | -4.45380 | 1.72638 | 1.52423 | C | 1.53688 | -3.99869 | -0.51901 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 2.11160 | -2.86516 | -2.24735 | H | 1.85175 | -1.44707 | -3.98948 |
| H | 0.58163 | -3.68684 | -2.42498 | H | 2.37136 | -0.36270 | -2.69289 |
| O | 0.37304 | -4.52009 | 0.13928 | O | -1.59268 | 0.69465 | -2.29752 |
| C | 2.40134 | -3.36339 | 0.59518 | C | 0.50192 | 1.47238 | -1.45814 |
| H | 2.10041 | -4.84808 | -0.93983 | H | 1.51842 | 1.44477 | -1.86079 |
| C | -0.33323 | -5.51660 | -0.58584 | H | 0.57300 | 1.17612 | -0.40479 |
| H | -0.85810 | -5.11098 | -1.46120 | C | 7.60175 | -2.09104 | 2.01855 |
| H | -1.07576 | -5.93827 | 0.09856 | H | 8.15311 | -1.92531 | 1.08569 |
| H | 0.33908 | -6.32106 | -0.91963 | H | 8.34733 | -2.23352 | 2.81510 |
| C | 2.82966 | -4.43208 | 1.61208 | H | 7.04491 | -3.03075 | 1.92105 |
| H | 1.78004 | -2.62127 | 1.11347 | C | 7.53148 | 0.37871 | 2.46367 |
| C | 3.62078 | -2.63515 | 0.01163 | H | 8.00477 | 0.63594 | 1.50723 |
| H | 1.95885 | -4.94774 | 2.02650 | H | 6.94124 | 1.24312 | 2.78974 |
| H | 3.38213 | -3.98332 | 2.44252 | H | 8.33804 | 0.24091 | 3.19899 |
| H | 3.47846 | -5.18393 | 1.14229 | C | 6.01677 | -1.17288 | 3.73583 |
| H | 4.20631 | -3.32710 | -0.61021 | H | 5.43745 | -2.10402 | 3.73615 |
| O | 4.46519 | -2.14818 | 1.06504 | H | 5.34361 | -0.36034 | 4.03524 |
| H | 3.30289 | -1.80681 | -0.63024 | H | 6.78605 | -1.26534 | 4.51672 |
| Si | 5.31295 | -0.69376 | 1.03585 | C | 6.67959 | -0.90420 | 2.36700 |
| C | 6.00474 | -0.44981 | -0.71305 | ---------- | | | |
| C | 4.12857 | 0.70976 | 1.50199 | | | | |
| C | 2.31636 | 2.75361 | 2.25999 | Compound **5.38** | | | |
| C | 4.50242 | 2.06995 | 1.47365 | This structure was assigned as incorrect. | | | |
| C | 2.82269 | 0.40891 | 1.93568 | B3LYP/6-31g(d) | | | |
| C | 1.92531 | 1.41375 | 2.30906 | Gas phase. | | | |
| C | 3.61035 | 3.07880 | 1.84552 | | | | |
| H | 5.50259 | 2.35647 | 1.15816 | Electronic Energy: -3261.31526002 har- | | | |
| H | 2.49944 | -0.62640 | 1.98901 | tree. | | | |
| H | 0.92223 | 1.14777 | 2.63302 | Free Energy: -3260.250253 hartree. | | | |
| H | 3.92617 | 4.11865 | 1.81033 | | | | |
| H | 1.61902 | 3.53796 | 2.54285 | N | 4.57263 | -3.29071 | -1.17005 |
| C | 7.05370 | -0.18601 | -3.33268 | C | 3.36347 | -3.25091 | -1.64748 |
| C | 6.67086 | -1.51901 | -1.35002 | O | 3.18800 | -2.32540 | -2.62527 |
| C | 5.87042 | 0.74929 | -1.43878 | C | 4.42083 | -1.73513 | -2.76952 |
| C | 6.39008 | 0.88377 | -2.72947 | C | 5.26779 | -2.31970 | -1.88662 |
| C | 7.18982 | -1.39182 | -2.63987 | C | 6.72767 | -2.05807 | -1.65757 |
| H | 6.78291 | -2.47125 | -0.83782 | H | 4.50946 | -0.95786 | -3.50859 |
| H | 5.34746 | 1.59432 | -1.00071 | C | 7.04259 | -1.71815 | -0.17935 |
| H | 6.27194 | 1.82337 | -3.26389 | O | 7.09693 | -1.00409 | -2.54221 |
| H | 7.69753 | -2.23363 | -3.10451 | H | 7.29061 | -2.97044 | -1.91948 |
| H | 7.45717 | -0.08402 | -4.33711 | C | 8.46995 | -0.97752 | -2.88232 |
| C | -0.40140 | 0.45609 | -2.16625 | H | 9.11614 | -0.79227 | -2.01206 |
| C | -0.76468 | -1.51320 | -3.67382 | H | 8.60117 | -0.15871 | -3.59435 |
| C | 1.55520 | -0.58216 | -3.38912 | H | 8.78552 | -1.91928 | -3.35758 |
| H | -0.92921 | -0.84046 | -4.52257 | H | 8.13416 | -1.61584 | -0.08583 |
| H | -1.73550 | -1.72539 | -3.22136 | H | 6.74883 | -2.57562 | 0.43637 |
| H | -0.35293 | -2.44799 | -4.06572 | C | 6.35938 | -0.46830 | 0.29127 |
| H | 1.45122 | 0.26798 | -4.07265 | C | 5.55917 | -0.38913 | 1.36748 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 6.51952 | 0.42111 | -0.31800 | C | 0.86293 | -3.37065 | 0.90432 |
| H | 5.38815 | -1.28115 | 1.97205 | C | -1.75455 | -3.19446 | 0.82486 |
| C | 4.85577 | 0.81828 | 1.77242 | H | -0.44562 | -2.72702 | 2.46976 |
| C | 3.98932 | 0.89280 | 2.79760 | C | -2.96477 | -2.85899 | 1.71057 |
| H | 5.03086 | 1.70816 | 1.16538 | H | -1.88341 | -2.81882 | -0.19110 |
| H | 3.80720 | 0.01362 | 3.41880 | H | -1.70559 | -4.28748 | 0.76413 |
| C | 3.17753 | 2.11049 | 3.15247 | O | -2.78619 | -3.59329 | 2.93034 |
| C | 1.67028 | 1.86360 | 2.98602 | C | -4.30504 | -3.24892 | 1.03650 |
| H | 3.48071 | 2.95343 | 2.51159 | H | -2.98599 | -1.78386 | 1.92893 |
| O | 3.35183 | 2.47279 | 4.52592 | C | -2.94581 | -2.84393 | 4.12776 |
| C | 4.62785 | 3.00578 | 4.81957 | H | -3.97585 | -2.48321 | 4.25737 |
| H | 4.83033 | 3.91752 | 4.23379 | H | -2.25893 | -1.98938 | 4.16218 |
| H | 5.43638 | 2.28607 | 4.62551 | H | -2.71143 | -3.52560 | 4.95123 |
| H | 4.62568 | 3.26201 | 5.88262 | C | -5.48638 | -3.21218 | 2.01663 |
| C | 1.22572 | 1.58346 | 1.54832 | H | -4.19982 | -4.28472 | 0.67733 |
| H | 1.13810 | 2.75127 | 3.34731 | C | -4.60428 | -2.39628 | -0.20633 |
| H | 1.37798 | 1.02732 | 3.63031 | H | -5.65979 | -2.19751 | 2.39078 |
| C | -0.24324 | 1.08299 | 1.49265 | H | -5.30626 | -3.87347 | 2.86774 |
| H | 1.86830 | 0.80642 | 1.11141 | H | -6.40542 | -3.54444 | 1.51854 |
| O | 1.36825 | 2.78237 | 0.79398 | H | -3.84753 | -2.55218 | -0.98479 |
| Si | 1.49432 | 2.96719 | -0.87798 | O | -4.65555 | -1.01692 | 0.14667 |
| C | 2.56063 | 4.54140 | -1.12531 | H | -5.56857 | -2.72033 | -0.62339 |
| C | 2.30415 | 1.44056 | -1.64904 | Si | -4.91637 | 0.30865 | -0.84983 |
| C | -0.21796 | 3.21772 | -1.63653 | C | -4.37763 | 1.75785 | 0.23333 |
| C | 1.90081 | 5.73276 | -0.39704 | C | -3.77495 | 0.16915 | -2.35264 |
| C | 2.67793 | 4.87142 | -2.62992 | C | -1.94372 | -0.10321 | -4.49433 |
| C | 3.97865 | 4.33214 | -0.55416 | C | -4.11283 | 0.56729 | -3.65898 |
| H | 4.50415 | 3.50749 | -1.05209 | C | -2.48359 | -0.36290 | -2.15386 |
| H | 3.95354 | 4.11728 | 0.52004 | C | -1.58005 | -0.50864 | -3.20827 |
| H | 4.58601 | 5.23836 | -0.69540 | C | -3.20922 | 0.44055 | -4.71664 |
| H | 1.70256 | 5.07728 | -3.08645 | H | -5.09446 | 0.98315 | -3.86630 |
| H | 3.14769 | 4.05740 | -3.19651 | H | -2.17122 | -0.67459 | -1.16029 |
| H | 3.29937 | 5.76717 | -2.77485 | H | -0.60727 | -0.95342 | -3.02032 |
| H | 0.90086 | 5.95013 | -0.79225 | H | -3.49831 | 0.76015 | -5.71495 |
| H | 2.50642 | 6.64259 | -0.52286 | H | -1.24465 | -0.21338 | -5.31969 |
| H | 1.80172 | 5.54250 | 0.67731 | C | -3.61503 | 3.94061 | 1.85973 |
| H | 1.67303 | 0.55025 | -1.53975 | C | -4.34764 | 1.64549 | 1.63582 |
| H | 2.45360 | 1.59513 | -2.72500 | C | -4.00774 | 2.99295 | -0.33050 |
| H | 3.28024 | 1.20939 | -1.20762 | C | -3.63521 | 4.07449 | 0.46996 |
| H | -0.79113 | 3.97053 | -1.08414 | C | -3.96938 | 2.72172 | 2.44166 |
| H | -0.80358 | 2.29159 | -1.63215 | H | -4.61448 | 0.70044 | 2.10066 |
| H | -0.14757 | 3.54614 | -2.68072 | H | -3.99726 | 3.11333 | -1.41185 |
| C | -0.38164 | -0.32144 | 2.04367 | H | -3.35588 | 5.01899 | 0.00953 |
| H | -0.58451 | 1.09292 | 0.45566 | H | -3.95122 | 2.60866 | 3.52286 |
| H | -0.88192 | 1.75270 | 2.07598 | H | -3.32159 | 4.77994 | 2.48508 |
| O | -0.47011 | -0.60074 | 3.22317 | C | 1.03474 | -3.32016 | -0.62453 |
| O | -0.35177 | -1.23687 | 1.04336 | C | 0.80775 | -4.84357 | 1.39024 |
| C | -0.43242 | -2.65251 | 1.38041 | C | 2.09688 | -2.68886 | 1.54684 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 0.45523 | -4.87498 | 2.42676 | H | 2.25329 | -5.02911 | -1.64021 |
| H | 1.79783 | -5.30838 | 1.36572 | H | 2.54029 | -4.32131 | -3.25721 |
| H | 0.12921 | -5.46128 | 0.79344 | H | -0.52181 | -4.47420 | -4.09011 |
| H | 3.02461 | -3.20158 | 1.27568 | H | -1.10571 | -2.90870 | -4.66291 |
| H | 1.99872 | -2.71188 | 2.63825 | C | -1.93881 | -3.49530 | -2.78301 |
| H | 2.18751 | -1.64548 | 1.23439 | C | -2.92451 | -2.57879 | -2.78271 |
| O | 0.30128 | -2.68659 | -1.35613 | H | -1.86631 | -4.20580 | -1.95431 |
| C | 2.20453 | -4.11172 | -1.26336 | H | -2.95250 | -1.84859 | -3.59651 |
| H | 1.79075 | -4.58237 | -2.16247 | C | -3.85451 | -2.35899 | -1.70041 |
| H | 2.59059 | -4.89054 | -0.60561 | C | -4.56350 | -1.22559 | -1.54941 |
| C | -7.58344 | 0.28745 | 0.03870 | H | -3.90421 | -3.11859 | -0.91331 |
| H | -7.31841 | 1.05572 | 0.77462 | H | -4.51940 | -0.44839 | -2.32061 |
| H | -8.66189 | 0.37653 | -0.15715 | C | -5.39040 | -0.91329 | -0.34721 |
| H | -7.40733 | -0.69044 | 0.49987 | C | -4.91910 | 0.32801 | 0.40249 |
| C | -7.12460 | 1.84619 | -1.86423 | H | -5.37560 | -1.78109 | 0.33779 |
| H | -6.63268 | 2.03211 | -2.82620 | O | -6.75580 | -0.64028 | -0.70511 |
| H | -6.83729 | 2.65475 | -1.18325 | C | -7.42660 | -1.79908 | -1.15731 |
| H | -8.20775 | 1.92799 | -2.03629 | H | -7.39331 | -2.60178 | -0.40171 |
| C | -7.24494 | -0.63716 | -2.27084 | H | -7.00040 | -2.19158 | -2.09441 |
| H | -7.10021 | -1.64502 | -1.86463 | H | -8.47000 | -1.51938 | -1.33421 |
| H | -8.31794 | -0.52745 | -2.48647 | C | -3.50470 | 0.24671 | 0.96419 |
| H | -6.71066 | -0.58731 | -3.22557 | H | -5.61920 | 0.50401 | 1.23179 |
| C | -6.79036 | 0.45584 | -1.27813 | H | -4.98840 | 1.20291 | -0.26321 |
| | | | | C | -3.21800 | 1.47181 | 1.84699 |
| | | | | H | -2.77400 | 0.20441 | 0.13539 |
| | | | | O | -3.39740 | -0.92389 | 1.76659 |
| | | | | Si | -1.94080 | -1.72140 | 2.10389 |
| | | | | C | -2.30571 | -2.57909 | 3.75649 |
| | | | | C | -1.53971 | -2.96090 | 0.75889 |
| | | | | C | -0.49390 | -0.53000 | 2.23389 |
| | | | | C | -1.05261 | -3.31460 | 4.23819 |
| | | | | C | -3.44571 | -3.58659 | 3.57999 |
| | | | | C | -2.71210 | -1.53749 | 4.80299 |
| | | | | H | -3.62910 | -1.00439 | 4.51719 |
| | | | | H | -1.92820 | -0.78309 | 4.96389 |
| | | | | H | -2.90190 | -2.01649 | 5.77669 |
| | | | | H | -3.18181 | -4.38979 | 2.87789 |
| | | | | H | -4.36421 | -3.11019 | 3.20889 |
| | | | | H | -3.69311 | -4.06589 | 4.54059 |
| | | | | H | -1.25111 | -3.84850 | 5.18129 |
| | | | | H | -0.21861 | -2.62370 | 4.42769 |
| | | | | H | -0.70661 | -4.06270 | 3.51029 |
| | | | | H | -2.29141 | -3.75599 | 0.67439 |
| | | | | H | -0.56931 | -3.44080 | 0.95359 |
| | | | | H | -1.45711 | -2.47790 | -0.22411 |
| | | | | H | 0.44800 | -1.09890 | 2.19659 |
| | | | | H | -0.48320 | 0.05080 | 3.16639 |
| | | | | H | -0.46750 | 0.18310 | 1.39769 |

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Compound **5.38**

This structure was assigned as incorrect.

M06-2X/6-31g(d)//M06-L/6-31g(d)

SMD implicit solvation in methanol was used.

Electronic Energy (M06-2X): -3260.17481960 hartree.

Free Energy Correction (M06-L): 1.18098 hartree.

| | | | |
|---|---|---|---|
| N | -0.70330 | -0.52550 | -3.34831 |
| C | -0.90900 | 0.45580 | -2.52391 |
| O | -0.27190 | 0.31260 | -1.32901 |
| C | 0.36970 | -0.89770 | -1.42121 |
| C | 0.10170 | -1.41500 | -2.64531 |
| C | 0.43809 | -2.76700 | -3.18311 |
| H | 0.92790 | -1.21080 | -0.54821 |
| C | -0.81521 | -3.46710 | -3.76331 |
| O | 1.02099 | -3.48580 | -2.09771 |
| H | 1.18149 | -2.68560 | -3.99821 |
| C | 1.76729 | -4.60830 | -2.52621 |
| H | 1.13029 | -5.38480 | -2.97701 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -2.93709 | 2.76121 | 1.13249 | H | 1.86759 | -4.45180 | 1.09229 |
| H | -2.32900 | 1.26171 | 2.45699 | H | 2.88840 | -2.22431 | 4.62909 |
| H | -4.05430 | 1.63321 | 2.53669 | H | 1.91559 | -4.25130 | 3.57139 |
| O | -3.51039 | 3.81511 | 1.34459 | C | -1.07379 | 2.95470 | -2.57071 |
| O | -1.90999 | 2.62120 | 0.26819 | C | -1.09459 | 5.42340 | -2.16651 |
| C | -1.27919 | 3.83160 | -0.24931 | C | -3.20439 | 4.13751 | -1.87041 |
| C | -1.68079 | 4.07980 | -1.73131 | H | -1.42048 | 6.21530 | -1.48141 |
| C | 0.20891 | 3.64070 | -0.01661 | H | -1.45099 | 5.68140 | -3.17091 |
| H | -1.65899 | 4.67730 | 0.33729 | H | -0.00149 | 5.41980 | -2.19611 |
| C | 0.58931 | 3.47670 | 1.44969 | H | -3.49059 | 4.25801 | -2.92251 |
| H | 0.56021 | 2.77310 | -0.58991 | H | -3.59009 | 5.00291 | -1.31871 |
| H | 0.74651 | 4.51520 | -0.40621 | H | -3.71289 | 3.24721 | -1.48451 |
| O | 0.29461 | 4.72040 | 2.09889 | O | -0.00289 | 3.08910 | -3.14371 |
| C | 2.07551 | 3.10799 | 1.59909 | C | -1.80760 | 1.62311 | -2.65641 |
| H | -0.02619 | 2.68470 | 1.91379 | H | -2.30290 | 1.57791 | -3.63551 |
| C | -0.40909 | 4.57390 | 3.31579 | H | -2.59910 | 1.55481 | -1.90011 |
| H | 0.14311 | 3.96810 | 4.05059 | C | 6.72300 | -1.24372 | -0.04711 |
| H | -0.54979 | 5.57940 | 3.72669 | H | 6.52750 | -1.36122 | -1.12191 |
| H | -1.39929 | 4.11370 | 3.16189 | H | 7.81660 | -1.22602 | 0.08139 |
| C | 2.61211 | 3.34999 | 3.00289 | H | 6.35199 | -2.14592 | 0.46089 |
| H | 2.64781 | 3.73089 | 0.89039 | C | 6.62760 | 1.24208 | -0.27171 |
| C | 2.29440 | 1.65200 | 1.20529 | H | 6.22131 | 2.19078 | 0.10479 |
| H | 2.09351 | 2.71699 | 3.73749 | H | 6.38160 | 1.17599 | -1.34091 |
| H | 2.49101 | 4.39519 | 3.30819 | H | 7.72440 | 1.30148 | -0.19301 |
| H | 3.68011 | 3.10619 | 3.05439 | C | 6.49970 | 0.18418 | 1.98619 |
| H | 1.92220 | 0.99520 | 2.01089 | H | 6.18870 | -0.68122 | 2.58739 |
| O | 3.68700 | 1.42569 | 1.00149 | H | 7.59470 | 0.26158 | 2.07589 |
| H | 1.73160 | 1.38580 | 0.29419 | H | 6.07120 | 1.08549 | 2.44609 |
| Si | 4.21110 | -0.02911 | 0.34289 | C | 6.10090 | 0.03739 | 0.51509 |
| C | 3.43810 | -1.41941 | 1.34439 | --- | | | |
| C | 3.71380 | -0.09411 | -1.46771 | | | | |
| C | 3.06470 | -0.10061 | -4.21611 | Compound **5.38** | | | |
| C | 3.92860 | -1.23281 | -2.26661 | This structure was assigned as correct. | | | |
| C | 3.17420 | 1.04439 | -2.09361 | B3LYP/6-31g(d) | | | |
| C | 2.85010 | 1.04339 | -3.44951 | SMD implicit solvation in methanol was used. | | | |
| C | 3.61100 | -1.23771 | -3.62331 | | | | |
| H | 4.35529 | -2.13801 | -1.82941 | | | | |
| H | 3.00901 | 1.95489 | -1.51221 | Electronic Energy: -3261.37099662 hartree. | | | |
| H | 2.43111 | 1.93699 | -3.90971 | | | | |
| H | 3.79299 | -2.13151 | -4.21991 | Free Energy: -3260.304187 hartree. | | | |
| H | 2.80860 | -0.10471 | -5.27511 | | | | |
| C | 2.33309 | -3.45991 | 2.95019 | N | 1.72707 | 3.48448 | -2.34562 |
| C | 3.42600 | -1.31761 | 2.74899 | C | 0.90550 | 2.47951 | -2.28844 |
| C | 2.85969 | -2.56341 | 0.77159 | O | 0.26733 | 2.36610 | -1.09324 |
| C | 2.31219 | -3.57401 | 1.56159 | C | 0.75212 | 3.40781 | -0.33222 |
| C | 2.88420 | -2.32431 | 3.54399 | C | 1.64474 | 4.08937 | -1.09142 |
| H | 3.84150 | -0.42921 | 3.23099 | C | 2.53019 | 5.24044 | -0.71432 |
| H | 2.81999 | -2.66461 | -0.31361 | H | 0.36142 | 3.49948 | 0.66784 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 4.03040 | 4.85820 | -0.85120 | H | 3.10556 | 1.02491 | 2.97948 |
| O | 2.18227 | 5.60342 | 0.62148 | H | 2.08507 | 0.95241 | 1.53237 |
| H | 2.33740 | 6.09021 | -1.38774 | H | -0.60596 | -0.99148 | 2.64864 |
| C | 2.52208 | 6.94017 | 0.97132 | H | -0.10439 | -2.64758 | 2.27687 |
| H | 3.60680 | 7.11172 | 0.96119 | H | 0.11454 | -1.35853 | 1.08071 |
| H | 2.15176 | 7.10198 | 1.98751 | C | 2.04416 | -3.35700 | -1.36288 |
| H | 2.04335 | 7.66340 | 0.29537 | H | 1.47272 | -3.41532 | 0.65936 |
| H | 4.62595 | 5.73831 | -0.57368 | H | 2.96269 | -4.30258 | 0.30328 |
| H | 4.22656 | 4.65899 | -1.91066 | O | 2.33604 | -4.22654 | -2.16747 |
| C | 4.41697 | 3.67320 | -0.01415 | O | 1.29948 | -2.27404 | -1.65790 |
| C | 4.77259 | 2.47405 | -0.51097 | C | 0.66741 | -2.13502 | -2.96909 |
| H | 4.36202 | 3.80292 | 1.06738 | C | 1.45758 | -1.08956 | -3.83266 |
| H | 4.81232 | 2.33655 | -1.59238 | C | -0.80193 | -1.81357 | -2.68075 |
| C | 5.07692 | 1.30630 | 0.30399 | H | 0.74683 | -3.09226 | -3.48727 |
| C | 5.33823 | 0.08346 | -0.19356 | C | -1.57796 | -2.98896 | -2.06156 |
| H | 5.05887 | 1.44746 | 1.38563 | H | -0.85164 | -0.93828 | -2.02593 |
| H | 5.35916 | -0.06626 | -1.27437 | H | -1.30356 | -1.55062 | -3.61723 |
| C | 5.61519 | -1.13937 | 0.63663 | O | -1.60104 | -4.03696 | -3.04928 |
| C | 4.71159 | -2.32829 | 0.27982 | C | -3.03125 | -2.60980 | -1.67236 |
| H | 5.50639 | -0.89865 | 1.70380 | H | -1.05459 | -3.35290 | -1.16689 |
| O | 6.95994 | -1.61631 | 0.40657 | C | -1.15873 | -5.31316 | -2.59773 |
| C | 7.96491 | -0.80505 | 0.99965 | H | -1.76161 | -5.68984 | -1.76171 |
| H | 7.84729 | -0.75667 | 2.09303 | H | -0.10389 | -5.29341 | -2.29369 |
| H | 7.96104 | 0.21958 | 0.60321 | H | -1.26747 | -5.99920 | -3.44385 |
| H | 8.92702 | -1.27126 | 0.76659 | C | -3.85717 | -3.84500 | -1.28855 |
| C | 3.22522 | -2.15447 | 0.60580 | H | -3.49691 | -2.14431 | -2.55381 |
| H | 5.08036 | -3.20755 | 0.82328 | C | -3.04683 | -1.57648 | -0.53437 |
| H | 4.81850 | -2.54312 | -0.79203 | H | -3.43769 | -4.34590 | -0.40612 |
| C | 2.41497 | -3.37753 | 0.10419 | H | -3.89137 | -4.56619 | -2.10984 |
| H | 2.84275 | -1.24613 | 0.12682 | H | -4.88684 | -3.56026 | -1.05144 |
| O | 3.08033 | -2.05319 | 2.02891 | H | -2.57081 | -2.00404 | 0.35909 |
| Si | 1.87493 | -1.17166 | 2.83680 | O | -4.39979 | -1.21552 | -0.21803 |
| C | 2.07691 | -1.69386 | 4.66539 | H | -2.48556 | -0.67887 | -0.81165 |
| C | 2.13918 | 0.68021 | 2.59416 | Si | -4.89319 | 0.27147 | 0.39794 |
| C | 0.16603 | -1.59268 | 2.15168 | C | -4.37775 | 0.38895 | 2.21768 |
| C | 1.80703 | -3.20535 | 4.81949 | C | -4.09593 | 1.63227 | -0.65577 |
| C | 1.07463 | -0.90999 | 5.53934 | C | -2.94514 | 3.61088 | -2.32782 |
| C | 3.51092 | -1.38973 | 5.14861 | C | -4.11016 | 1.50648 | -2.06166 |
| H | 4.26388 | -1.93836 | 4.56971 | C | -3.47336 | 2.77460 | -0.11766 |
| H | 3.63056 | -1.68280 | 6.20266 | C | -2.91054 | 3.75531 | -0.93954 |
| H | 3.75115 | -0.32104 | 5.08103 | C | -3.54438 | 2.47960 | -2.88833 |
| H | 0.03366 | -1.09352 | 5.24328 | H | -4.56286 | 0.63284 | -2.52382 |
| H | 1.24774 | 0.17278 | 5.49529 | H | -3.41442 | 2.90655 | 0.95853 |
| H | 1.16892 | -1.21123 | 6.59346 | H | -2.43985 | 4.62817 | -0.49400 |
| H | 0.77863 | -3.47115 | 4.54418 | H | -3.57198 | 2.35490 | -3.96815 |
| H | 1.95372 | -3.51630 | 5.86490 | H | -2.50664 | 4.37180 | -2.96867 |
| H | 2.48366 | -3.80786 | 4.20095 | C | -3.67588 | 0.44746 | 4.96413 |
| H | 1.35342 | 1.24775 | 3.11013 | C | -3.87607 | -0.75408 | 2.87189 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | -4.52800 | 1.55991 | 2.98965 | C | -0.15590 | 0.64810 | -2.75200 |
| C | -4.18005 | 1.59205 | 4.34230 | O | 0.05590 | 0.39070 | -1.43310 |
| C | -3.52834 | -0.72869 | 4.22569 | C | 0.39500 | -0.93840 | -1.38760 |
| H | -3.76368 | -1.68443 | 2.32175 | C | 0.36840 | -1.41050 | -2.65720 |
| H | -4.92788 | 2.46499 | 2.54013 | C | 0.58390 | -2.80150 | -3.14340 |
| H | -4.30584 | 2.51079 | 4.91005 | H | 0.62450 | -1.34449 | -0.41140 |
| H | -3.14702 | -1.62832 | 4.70287 | C | -0.68680 | -3.34080 | -3.84270 |
| H | -3.40582 | 0.47035 | 6.01696 | O | 0.94751 | -3.57829 | -2.00590 |
| C | 1.61988 | 0.21741 | -3.03152 | H | 1.41230 | -2.81649 | -3.87560 |
| C | 0.72722 | -0.88004 | -5.17426 | C | 1.61661 | -4.77239 | -2.36030 |
| C | 2.86941 | -1.64023 | -4.13240 | H | 0.98061 | -5.44620 | -2.95560 |
| H | 0.56632 | -1.84800 | -5.66267 | H | 1.88711 | -5.27919 | -1.42890 |
| H | 1.34141 | -0.26911 | -5.84483 | H | 2.53481 | -4.55939 | -2.93240 |
| H | -0.24507 | -0.39248 | -5.07221 | H | -0.46939 | -4.34410 | -4.23320 |
| H | 3.42856 | -0.92415 | -4.74493 | H | -0.87910 | -2.69100 | -4.70690 |
| H | 2.79369 | -2.57928 | -4.69014 | C | -1.85250 | -3.34880 | -2.91340 |
| H | 3.44494 | -1.82072 | -3.22271 | C | -2.74370 | -2.34340 | -2.82240 |
| O | 2.50298 | 0.32148 | -2.19331 | H | -1.90379 | -4.16610 | -2.18750 |
| C | 0.68112 | 1.40334 | -3.28992 | H | -2.66870 | -1.50280 | -3.52160 |
| H | -0.36164 | 1.07048 | -3.27871 | C | -3.73320 | -2.23080 | -1.77640 |
| H | 0.88401 | 1.78792 | -4.29615 | C | -4.49050 | -1.14080 | -1.56200 |
| C | -7.40044 | 1.56024 | 0.77681 | H | -3.80200 | -3.06540 | -1.07040 |
| H | -7.02727 | 2.43233 | 0.22469 | H | -4.43870 | -0.29610 | -2.25350 |
| H | -8.49523 | 1.55048 | 0.67081 | C | -5.36190 | -0.95320 | -0.36570 |
| H | -7.18030 | 1.71682 | 1.83943 | C | -4.94490 | 0.25100 | 0.47180 |
| C | -7.23742 | 0.04903 | -1.22117 | H | -5.33380 | -1.86810 | 0.25530 |
| H | -6.84491 | -0.88074 | -1.65014 | O | -6.72770 | -0.69881 | -0.73630 |
| H | -6.91005 | 0.87930 | -1.85771 | C | -7.32600 | -1.82291 | -1.34840 |
| H | -8.33474 | 0.00299 | -1.28679 | H | -7.29480 | -2.70661 | -0.68830 |
| C | -7.36208 | -0.93468 | 1.08447 | H | -6.83800 | -2.08941 | -2.29930 |
| H | -7.10056 | -0.84578 | 2.14586 | H | -8.37110 | -1.56421 | -1.54670 |
| H | -8.45997 | -0.95859 | 1.01892 | C | -3.53570 | 0.18170 | 1.04670 |
| H | -6.99187 | -1.90418 | 0.72957 | H | -5.66130 | 0.35600 | 1.29960 |
| C | -6.80618 | 0.23800 | 0.24800 | H | -5.03170 | 1.15940 | -0.14510 |
| | | | | C | -3.27680 | 1.39310 | 1.95830 |
| | | | | H | -2.79860 | 0.17130 | 0.22260 |
| | | | | O | -3.41610 | -1.00690 | 1.82140 |
| | | | | Si | -1.94700 | -1.78690 | 2.14030 |
| | | | | C | -2.25690 | -2.59250 | 3.82920 |
| | | | | C | -1.59100 | -3.06340 | 0.81720 |
| | | | | C | -0.50530 | -0.58120 | 2.17320 |
| | | | | C | -0.99820 | -3.32970 | 4.29170 |
| | | | | C | -3.41399 | -3.59070 | 3.72090 |
| | | | | C | -2.61590 | -1.51580 | 4.85680 |
| | | | | H | -3.52720 | -0.96870 | 4.57860 |
| | | | | H | -1.81070 | -0.77710 | 4.98000 |
| | | | | H | -2.79330 | -1.96620 | 5.84630 |
| | | | | H | -3.18419 | -4.41580 | 3.03190 |

---

Compound **5.38**

This structure was assigned as correct.

M06-2X/6-31g(d)//M06-L/6-31g(d)

SMD implicit solvation in methanol was used.

Electronic Energy (M06-2X): -3260.17787821 hartree.

Free Energy Correction (M06-L): 1.07907 hartree.

| | | | |
|---|---|---|---|
| N | 0.00190 | -0.38550 | -3.52190 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -4.33930 | -3.11320 | 3.36970 | H | 4.55510 | -2.05929 | -1.69430 |
| H | -3.63159 | -4.04060 | 4.70280 | H | 4.22700 | -2.08609 | -4.13150 |
| H | -1.16480 | -3.81390 | 5.26730 | H | 2.78070 | 1.96271 | -3.99770 |
| H | -0.14200 | -2.64980 | 4.41020 | H | 3.33370 | -0.07989 | -5.29990 |
| H | -0.70059 | -4.11910 | 3.58640 | C | 2.30651 | -3.43079 | 2.90570 |
| H | -2.38650 | -3.81340 | 0.72220 | C | 3.36960 | -1.26809 | 2.77860 |
| H | -0.65450 | -3.59830 | 1.03380 | C | 2.86010 | -2.47209 | 0.75990 |
| H | -1.46320 | -2.58550 | -0.16290 | C | 2.31201 | -3.50879 | 1.51440 |
| H | 0.43930 | -1.14350 | 2.11910 | C | 2.82810 | -2.30219 | 3.53790 |
| H | -0.46030 | 0.03690 | 3.07980 | H | 3.76320 | -0.38799 | 3.29190 |
| H | -0.52050 | 0.09480 | 1.30600 | H | 2.83950 | -2.55229 | -0.32820 |
| C | -2.98970 | 2.69130 | 1.26220 | H | 1.88971 | -4.38059 | 1.01460 |
| H | -2.39740 | 1.18240 | 2.58300 | H | 2.81160 | -2.22939 | 4.62510 |
| H | -4.12420 | 1.54150 | 2.63760 | H | 1.89191 | -4.24529 | 3.49810 |
| O | -3.50711 | 3.76160 | 1.53060 | C | -1.86660 | 2.39860 | -2.41940 |
| O | -2.02820 | 2.52530 | 0.33470 | C | -1.35461 | 4.88600 | -2.55200 |
| C | -1.47070 | 3.69740 | -0.32640 | C | -3.54700 | 4.08510 | -1.68930 |
| C | -2.05240 | 3.77080 | -1.76960 | H | -1.47261 | 5.83940 | -2.02180 |
| C | 0.03610 | 3.57280 | -0.18030 | H | -1.81281 | 4.99940 | -3.54170 |
| H | -1.82121 | 4.58850 | 0.20980 | H | -0.28221 | 4.72280 | -2.69670 |
| C | 0.50550 | 3.57860 | 1.27140 | H | -3.97361 | 4.16770 | -2.69600 |
| H | 0.39380 | 2.65620 | -0.66220 | H | -3.70341 | 5.03990 | -1.17380 |
| H | 0.51669 | 4.41770 | -0.69120 | H | -4.10700 | 3.31030 | -1.15780 |
| O | 0.18479 | 4.86980 | 1.80230 | O | -2.75550 | 1.56040 | -2.39200 |
| C | 2.01280 | 3.27221 | 1.36360 | C | -0.54300 | 2.03610 | -3.08620 |
| H | -0.04950 | 2.81740 | 1.85020 | H | 0.26160 | 2.73400 | -2.82890 |
| C | -0.38981 | 4.82860 | 3.09380 | H | -0.68730 | 2.11630 | -4.17180 |
| H | -0.65001 | 5.85870 | 3.35930 | C | 6.78670 | -1.05679 | 0.15040 |
| H | -1.30661 | 4.21630 | 3.11050 | H | 6.65840 | -1.16019 | -0.93560 |
| H | 0.30419 | 4.43350 | 3.85150 | H | 7.86960 | -1.00519 | 0.34430 |
| C | 2.64819 | 3.74371 | 2.66320 | H | 6.41800 | -1.98029 | 0.62070 |
| H | 2.51240 | 3.78991 | 0.52660 | C | 6.61140 | 1.42711 | -0.04400 |
| C | 2.24550 | 1.77511 | 1.18080 | H | 6.15300 | 2.35431 | 0.32690 |
| H | 2.23180 | 3.20951 | 3.52890 | H | 7.70020 | 1.52301 | 0.09140 |
| H | 2.49539 | 4.81691 | 2.81980 | H | 6.42130 | 1.37161 | -1.12520 |
| H | 3.72880 | 3.55811 | 2.65030 | C | 6.40750 | 0.32951 | 2.18760 |
| H | 1.87340 | 1.23331 | 2.06880 | H | 6.11290 | -0.56269 | 2.75670 |
| O | 3.64010 | 1.53241 | 1.02270 | H | 7.49150 | 0.46121 | 2.33220 |
| H | 1.68900 | 1.38391 | 0.31290 | H | 5.91100 | 1.19861 | 2.64130 |
| Si | 4.21190 | 0.07281 | 0.41840 | C | 6.08850 | 0.19121 | 0.69650 |
| C | 3.41360 | -1.33529 | 1.37260 | --- | | | |
| C | 3.84450 | -0.02709 | -1.42070 | | | | |
| C | 3.47810 | -0.06509 | -4.22010 | Compound **5.38** | | | |
| C | 3.34920 | 1.09621 | -2.10680 | This structure was assigned as correct. | | | |
| C | 4.15490 | -1.16849 | -2.18270 | B3LYP/6-31g(d) | | | |
| C | 3.97460 | -1.19039 | -3.56450 | Gas phase. | | | |
| C | 3.16570 | 1.07921 | -3.48830 | | | | |
| H | 3.11190 | 2.00671 | -1.55050 | | | | |

Electronic Energy: -3261.31363326 hartree.
Free Energy: -3260.248080 hartree.

| | | | |
|---|---|---|---|
| N | -0.22970 | -1.71042 | -3.56858 |
| C | 0.07162 | -0.58400 | -3.00286 |
| O | 0.43250 | -0.70240 | -1.69499 |
| C | 0.33163 | -2.04849 | -1.42751 |
| C | -0.07154 | -2.66440 | -2.56530 |
| C | -0.41473 | -4.10453 | -2.80069 |
| H | 0.58018 | -2.36767 | -0.43038 |
| C | -1.88994 | -4.24548 | -3.27590 |
| O | -0.14978 | -4.79723 | -1.58486 |
| H | 0.23353 | -4.50505 | -3.59966 |
| C | -0.01924 | -6.19741 | -1.72814 |
| H | -0.95507 | -6.67849 | -2.04728 |
| H | 0.25567 | -6.59096 | -0.74589 |
| H | 0.77004 | -6.45820 | -2.45092 |
| H | -2.07837 | -5.30067 | -3.51546 |
| H | -1.97273 | -3.68303 | -4.21229 |
| C | -2.88723 | -3.73958 | -2.27201 |
| C | -3.48449 | -2.53742 | -2.34994 |
| H | -3.07511 | -4.37220 | -1.40434 |
| H | -3.26206 | -1.88699 | -3.19513 |
| C | -4.36904 | -1.99004 | -1.33253 |
| C | -4.85389 | -0.73589 | -1.35511 |
| H | -4.60579 | -2.63754 | -0.48663 |
| H | -4.60922 | -0.08311 | -2.19253 |
| C | -5.69601 | -0.12176 | -0.27057 |
| C | -5.10405 | 1.19333 | 0.25572 |
| H | -5.80246 | -0.83119 | 0.56510 |
| O | -6.99861 | 0.23489 | -0.75691 |
| C | -7.83517 | -0.87386 | -1.01791 |
| H | -8.00870 | -1.47260 | -0.10835 |
| H | -7.42174 | -1.53582 | -1.79212 |
| H | -8.79176 | -0.47249 | -1.36415 |
| C | -3.73528 | 1.07666 | 0.93048 |
| H | -5.81484 | 1.61934 | 0.97379 |
| H | -5.03366 | 1.89786 | -0.58376 |
| C | -3.20896 | 2.47195 | 1.34242 |
| H | -3.02155 | 0.61404 | 0.23787 |
| O | -3.87663 | 0.27742 | 2.10750 |
| Si | -2.71600 | -0.71291 | 2.82265 |
| C | -3.41972 | -1.05583 | 4.56973 |
| C | -2.49301 | -2.31258 | 1.84349 |
| C | -1.03310 | 0.15650 | 2.89934 |
| C | -2.47260 | -1.99662 | 5.34598 |
| C | -4.80811 | -1.72079 | 4.45062 |
| C | -3.56744 | 0.26864 | 5.34836 |
| H | -4.23343 | 0.96697 | 4.82970 |
| H | -2.60172 | 0.76879 | 5.49452 |
| H | -3.99044 | 0.08137 | 6.34614 |
| H | -4.75709 | -2.68621 | 3.93179 |
| H | -5.51304 | -1.08341 | 3.90580 |
| H | -5.22917 | -1.90985 | 5.44903 |
| H | -2.86828 | -2.19132 | 6.35346 |
| H | -1.47150 | -1.56421 | 5.46932 |
| H | -2.35919 | -2.96820 | 4.84916 |
| H | -3.40707 | -2.91675 | 1.83929 |
| H | -1.68916 | -2.92161 | 2.27528 |
| H | -2.22502 | -2.11242 | 0.79992 |
| H | -0.25994 | -0.52745 | 3.26967 |
| H | -1.04159 | 1.03587 | 3.55371 |
| H | -0.71781 | 0.48167 | 1.89997 |
| C | -2.62605 | 3.33543 | 0.24125 |
| H | -2.40453 | 2.32615 | 2.07159 |
| H | -3.99844 | 3.04717 | 1.83323 |
| O | -2.88427 | 4.50754 | 0.06932 |
| O | -1.70638 | 2.64484 | -0.48299 |
| C | -0.87879 | 3.35884 | -1.44487 |
| C | -1.35766 | 3.02334 | -2.90023 |
| C | 0.56772 | 3.00272 | -1.08473 |
| H | -1.03911 | 4.42955 | -1.30235 |
| C | 1.05450 | 3.64716 | 0.22592 |
| H | 0.65733 | 1.91521 | -1.02016 |
| H | 1.23900 | 3.35118 | -1.87727 |
| O | 0.99970 | 5.06552 | 0.03826 |
| C | 2.50440 | 3.23278 | 0.58718 |
| H | 0.38299 | 3.35590 | 1.04818 |
| C | 0.29258 | 5.79833 | 1.02908 |
| H | 0.37230 | 6.85212 | 0.74719 |
| H | -0.76975 | 5.52285 | 1.05964 |
| H | 0.72947 | 5.66908 | 2.02881 |
| C | 3.04274 | 4.02304 | 1.78744 |
| H | 3.13107 | 3.47619 | -0.28396 |
| C | 2.63530 | 1.72146 | 0.83862 |
| H | 2.43835 | 3.83822 | 2.68585 |
| H | 3.03587 | 5.09612 | 1.58089 |
| H | 4.06894 | 3.71794 | 2.00715 |
| H | 2.04511 | 1.43422 | 1.72174 |
| O | 4.00881 | 1.39746 | 1.06363 |
| H | 2.25060 | 1.14474 | -0.01050 |
| Si | 4.67907 | -0.12389 | 0.84479 |
| C | 3.56976 | -1.40240 | 1.70123 |
| C | 4.80224 | -0.46903 | -1.01407 |
| C | 5.05100 | -0.87502 | -3.80684 |

| | | | |
|---|---|---|---|
| C | 4.54686 | 0.56767 | -1.93208 |
| C | 5.20042 | -1.71297 | -1.54297 |
| C | 5.32213 | -1.91690 | -2.91877 |
| C | 4.66647 | 0.37073 | -3.30923 |
| H | 4.26248 | 1.54947 | -1.56285 |
| H | 5.42460 | -2.54206 | -0.87598 |
| H | 5.62987 | -2.88872 | -3.29640 |
| H | 4.46601 | 1.19166 | -3.99368 |
| H | 5.14407 | -1.03184 | -4.87834 |
| C | 1.88027 | -3.24404 | 3.03938 |
| C | 3.19233 | -1.21104 | 3.04665 |
| C | 3.05610 | -2.53734 | 1.04643 |
| C | 2.22349 | -3.44836 | 1.70212 |
| C | 2.36486 | -2.11875 | 3.71029 |
| H | 3.54119 | -0.33454 | 3.58654 |
| H | 3.29104 | -2.71103 | 0.00068 |
| H | 1.83659 | -4.30874 | 1.16144 |
| H | 2.09825 | -1.94765 | 4.75038 |
| H | 1.23725 | -3.95310 | 3.55452 |
| C | -1.32984 | 1.49530 | -3.13043 |
| C | -0.47113 | 3.77204 | -3.92115 |
| C | -2.80979 | 3.51297 | -3.07510 |
| H | -0.48172 | 4.84590 | -3.70375 |
| H | -0.86569 | 3.63755 | -4.93441 |
| H | 0.57247 | 3.44844 | -3.92379 |
| H | -3.14354 | 3.34139 | -4.10379 |
| H | -2.87720 | 4.58337 | -2.85923 |
| H | -3.49691 | 2.98087 | -2.41723 |
| O | -2.33597 | 0.82648 | -3.01150 |
| C | -0.01353 | 0.79564 | -3.55516 |
| H | 0.86877 | 1.37460 | -3.27646 |
| H | -0.02927 | 0.72643 | -4.64928 |
| C | 7.17160 | -1.34139 | 1.48718 |
| H | 7.31625 | -1.62954 | 0.43959 |
| H | 8.16882 | -1.26850 | 1.94455 |
| H | 6.63803 | -2.15534 | 1.99375 |
| C | 7.22018 | 1.09986 | 0.86845 |
| H | 6.73586 | 2.07869 | 0.95643 |
| H | 8.23235 | 1.18784 | 1.28913 |
| H | 7.32414 | 0.87083 | -0.19831 |
| C | 6.34431 | 0.38743 | 3.11150 |
| H | 5.85770 | -0.39404 | 3.70582 |
| H | 7.35584 | 0.52410 | 3.52079 |
| H | 5.79620 | 1.32438 | 3.26167 |
| C | 6.42875 | 0.00518 | 1.61857 |

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Compound **5.4**

This structure was assigned as correct.

Molecular Mechanics (OPLS-2005), gas phase.

Energy: -497.861664 kJ.

| | | | |
|---|---|---|---|
| C | 1.53810 | 8.76620 | -3.57520 |
| C | 1.74310 | 7.24880 | -3.80320 |
| H | 1.33020 | 9.21180 | -4.54870 |
| H | 0.62870 | 8.93750 | -3.00200 |
| H | 2.76760 | 7.08140 | -4.12390 |
| H | 1.13890 | 6.93040 | -4.65110 |
| C | 1.39110 | 6.35370 | -2.59260 |
| O | 0.04860 | 6.58680 | -2.15280 |
| H | 2.01540 | 6.66280 | -1.75830 |
| C | 1.66230 | 4.83410 | -2.78810 |
| Si | -1.44200 | 6.44450 | -2.96700 |
| C | -1.66230 | 7.81360 | -4.25080 |
| C | -1.61640 | 4.75730 | -3.79750 |
| C | -2.79700 | 6.63870 | -1.63270 |
| H | -0.96750 | 4.66650 | -4.66700 |
| H | -2.63490 | 4.59470 | -4.14660 |
| H | -1.37850 | 3.94720 | -3.10930 |
| H | -2.64670 | 7.76190 | -4.71320 |
| H | -1.57320 | 8.80070 | -3.79950 |
| H | -0.93140 | 7.75020 | -5.05390 |
| C | 1.29330 | 4.06670 | -1.50080 |
| C | 3.10690 | 4.50310 | -3.27240 |
| H | 1.00020 | 4.49190 | -3.57680 |
| H | 0.28600 | 4.31100 | -1.16760 |
| H | 1.98110 | 4.30770 | -0.69070 |
| H | 1.31010 | 2.98770 | -1.64430 |
| H | 3.21760 | 4.95220 | -4.25960 |
| C | 3.42180 | 2.98720 | -3.43460 |
| O | 4.03910 | 5.07460 | -2.35290 |
| H | 3.32970 | 2.50760 | -2.46350 |
| C | 4.84340 | 2.76460 | -3.93830 |
| C | 2.44330 | 2.27280 | -4.38370 |
| H | 2.42900 | 2.74280 | -5.36780 |
| H | 1.42440 | 2.27500 | -3.99740 |
| H | 2.72650 | 1.22830 | -4.51980 |
| C | 5.90680 | 2.33530 | -3.23050 |
| H | 4.99620 | 2.98750 | -4.98510 |
| H | 6.83790 | 2.22930 | -3.76970 |
| C | 5.91260 | 2.02570 | -1.81220 |
| C | 7.00500 | 1.57780 | -1.17500 |
| H | 5.01880 | 2.16220 | -1.22270 |
| H | 6.97870 | 1.36240 | -0.11630 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 7.93960 | 1.42010 | -1.69380 | O | 2.94880 | 9.95880 | 1.59110 |
| C | 5.06920 | 5.82860 | -2.79190 | Si | 4.28970 | 9.94190 | 2.61720 |
| O | 5.27120 | 6.08410 | -3.97860 | C | 5.00170 | 11.71140 | 2.61250 |
| C | 5.96250 | 6.34330 | -1.73400 | C | 3.71740 | 9.47790 | 4.35100 |
| C | 6.01270 | 6.03350 | -0.41890 | C | 5.57010 | 8.72060 | 1.97040 |
| H | 6.68240 | 7.06700 | -2.08600 | H | 2.79500 | 9.99670 | 4.60880 |
| C | 5.21460 | 5.09190 | 0.34950 | H | 3.53520 | 8.40990 | 4.43810 |
| H | 6.77550 | 6.56150 | 0.13510 | H | 4.46060 | 9.74490 | 5.09920 |
| C | 5.44190 | 4.90070 | 1.65860 | H | 5.22160 | 7.69580 | 2.07500 |
| H | 4.42430 | 4.52000 | -0.10860 | H | 6.50930 | 8.79980 | 2.51510 |
| C | 4.66680 | 3.96290 | 2.56440 | H | 5.78280 | 8.89570 | 0.91680 |
| H | 6.23090 | 5.45580 | 2.14750 | C | 3.04860 | 9.22630 | -1.47870 |
| C | 5.58800 | 2.84630 | 3.07400 | C | 1.28400 | 10.74450 | -0.44390 |
| H | 3.88000 | 3.48620 | 1.97780 | H | 1.10160 | 8.64240 | -0.79430 |
| C | 4.01760 | 4.73910 | 3.73460 | H | 0.54830 | 10.88250 | 0.34290 |
| H | 5.04760 | 2.15360 | 3.71970 | H | 0.78140 | 10.97820 | -1.38140 |
| H | 6.42350 | 3.25190 | 3.64520 | H | 2.05900 | 11.49520 | -0.28640 |
| H | 6.00150 | 2.27090 | 2.24530 | C | 2.70350 | 9.57470 | -2.94690 |
| C | 2.92060 | 5.73090 | 3.29400 | H | 3.49370 | 8.23300 | -1.44770 |
| O | 5.03840 | 5.47360 | 4.39200 | H | 3.84220 | 9.89440 | -1.14000 |
| H | 3.58480 | 4.02500 | 4.43850 | C | 3.96270 | 9.56590 | -3.82890 |
| Si | 5.31650 | 5.45780 | 6.05830 | H | 2.37370 | 10.61390 | -2.95020 |
| C | 5.54070 | 3.67460 | 6.63070 | H | 4.44480 | 8.59060 | -3.84630 |
| C | 6.90530 | 6.46550 | 6.37530 | H | 4.69940 | 10.28210 | -3.46390 |
| C | 3.83460 | 6.24220 | 6.91880 | H | 3.72810 | 9.83840 | -4.85820 |
| H | 3.96910 | 6.26230 | 7.99920 | C | -2.62990 | 5.52660 | -0.58360 |
| H | 3.68250 | 7.26890 | 6.59040 | H | -1.64560 | 5.56720 | -0.11930 |
| H | 2.91770 | 5.69210 | 6.71130 | H | -2.73850 | 4.53700 | -1.02940 |
| H | 4.65500 | 3.07390 | 6.43020 | H | -3.37170 | 5.61200 | 0.21130 |
| H | 5.73440 | 3.62370 | 7.70110 | C | -2.64350 | 8.01610 | -0.96300 |
| H | 6.37980 | 3.19940 | 6.12520 | H | -2.80120 | 8.82650 | -1.67550 |
| H | 3.31120 | 6.38370 | 2.51600 | H | -1.64560 | 8.14740 | -0.54500 |
| H | 2.64910 | 6.35700 | 4.14220 | H | -3.36080 | 8.14950 | -0.15260 |
| C | 1.63240 | 5.05940 | 2.80740 | C | -4.18950 | 6.53200 | -2.27910 |
| O | 1.26280 | 4.02660 | 3.36330 | H | -4.34100 | 7.30360 | -3.03450 |
| C | 0.86090 | 5.60920 | 1.67900 | H | -4.33500 | 5.56560 | -2.76260 |
| C | 0.75240 | 6.89290 | 1.27360 | H | -4.97990 | 6.64550 | -1.53630 |
| H | 0.32330 | 4.86740 | 1.10940 | C | 7.24010 | 6.44140 | 7.87630 |
| C | 1.30300 | 8.18120 | 1.87470 | H | 8.14130 | 7.01640 | 8.09120 |
| H | 0.13800 | 7.05060 | 0.40070 | H | 6.43080 | 6.86530 | 8.47180 |
| C | 2.35730 | 8.84560 | 0.94560 | H | 7.40930 | 5.42410 | 8.23090 |
| H | 1.80250 | 7.95240 | 2.80910 | C | 6.68040 | 7.91420 | 5.91300 |
| C | 0.14310 | 9.10320 | 2.27500 | H | 7.58230 | 8.51610 | 6.02680 |
| H | 0.51080 | 10.05960 | 2.64860 | H | 6.38860 | 7.95060 | 4.86270 |
| H | -0.45430 | 8.65180 | 3.06750 | H | 5.89080 | 8.39570 | 6.49010 |
| H | -0.52850 | 9.29650 | 1.43920 | C | 8.05630 | 5.84010 | 5.56890 |
| C | 1.88340 | 9.31970 | -0.46020 | H | 7.82580 | 5.82240 | 4.50240 |
| H | 3.13390 | 8.09300 | 0.79870 | H | 8.24730 | 4.81170 | 5.87680 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 8.98380 | 6.39860 | 5.69690 | H | 2.98000 | 3.97900 | -4.32830 |
| C | 3.92120 | 12.68070 | 3.12090 | H | 3.62730 | 5.17700 | -0.76840 |
| H | 3.62150 | 12.44400 | 4.14240 | C | 4.84810 | 4.02170 | -2.05260 |
| H | 3.02510 | 12.63100 | 2.50000 | O | 2.65050 | 3.42590 | -1.31430 |
| H | 4.27250 | 13.71270 | 3.11120 | H | 4.72680 | 3.33650 | -2.88850 |
| C | 6.23910 | 11.77840 | 3.52460 | C | 5.46950 | 3.28520 | -0.87090 |
| H | 5.99330 | 11.51560 | 4.55380 | C | 5.82360 | 5.12250 | -2.50460 |
| H | 6.66690 | 12.78120 | 3.53790 | H | 5.89580 | 5.92060 | -1.76500 |
| H | 7.02010 | 11.09510 | 3.18990 | H | 5.52570 | 5.56660 | -3.45380 |
| C | 5.39230 | 12.08180 | 1.17140 | H | 6.82530 | 4.71710 | -2.65180 |
| H | 5.77990 | 13.09890 | 1.11090 | C | 5.70140 | 1.96530 | -0.74500 |
| H | 4.53340 | 12.01590 | 0.50160 | H | 5.74400 | 3.91710 | -0.03830 |
| H | 6.16000 | 11.41290 | 0.78120 | H | 6.15560 | 1.64280 | 0.18180 |
| | | | | C | 5.38540 | 0.94960 | -1.73050 |
| ---------- | | | | C | 5.66240 | -0.34880 | -1.53830 |
| | | | | H | 4.90560 | 1.22460 | -2.65740 |
| Compound **5.4** | | | | H | 5.41450 | -1.08590 | -2.28830 |
| This structure was assigned as ambiguous. | | | | H | 6.13940 | -0.69780 | -0.63360 |
| | | | | C | 2.06430 | 3.33900 | -0.11500 |
| Molecular Mechanics (OPLS-2005), gas phase. | | | | O | 1.84360 | 4.30070 | 0.61890 |
| | | | | C | 1.68150 | 1.95410 | 0.20120 |
| Energy: -496.159698 kJ. | | | | C | 1.72970 | 1.42550 | 1.44430 |
| | | | | H | 1.31970 | 1.35210 | -0.61870 |
| C | 3.16020 | 8.27990 | -1.49080 | C | 2.31210 | 2.05130 | 2.62170 |
| C | 2.05440 | 7.31760 | -1.01160 | H | 1.39270 | 0.40540 | 1.55470 |
| H | 4.08080 | 7.72860 | -1.67980 | C | 3.61200 | 2.39330 | 2.68710 |
| H | 2.85000 | 8.68700 | -2.45440 | H | 1.66950 | 2.26890 | 3.46290 |
| H | 1.19230 | 7.90210 | -0.69030 | C | 4.28680 | 3.08120 | 3.86100 |
| H | 2.38050 | 6.78720 | -0.11990 | H | 4.25560 | 2.18130 | 1.84490 |
| C | 1.59110 | 6.30130 | -2.08430 | C | 5.14110 | 2.07360 | 4.64180 |
| O | 0.97400 | 7.05040 | -3.11610 | H | 3.50650 | 3.42880 | 4.54000 |
| H | 0.84660 | 5.64240 | -1.63390 | C | 5.12160 | 4.30530 | 3.40450 |
| C | 2.71300 | 5.42950 | -2.70930 | H | 4.53110 | 1.25160 | 5.01700 |
| Si | -0.69470 | 7.15400 | -3.35820 | H | 5.61980 | 2.54610 | 5.49970 |
| C | -1.32870 | 5.45690 | -3.88100 | H | 5.92240 | 1.64490 | 4.01390 |
| C | -1.52220 | 7.68690 | -1.74960 | C | 4.29400 | 5.39600 | 2.69280 |
| C | -0.99140 | 8.44030 | -4.73470 | O | 6.11420 | 3.85140 | 2.49180 |
| H | -1.33460 | 6.97410 | -0.94810 | H | 5.60720 | 4.74660 | 4.27680 |
| H | -2.60110 | 7.77520 | -1.86720 | Si | 7.78820 | 4.05440 | 2.65260 |
| H | -1.15090 | 8.65470 | -1.41800 | C | 8.60270 | 2.85420 | 1.44960 |
| H | -0.83730 | 5.11740 | -4.79150 | C | 8.27960 | 5.84790 | 2.19580 |
| H | -2.40030 | 5.47480 | -4.07370 | C | 8.32280 | 3.65630 | 4.41730 |
| H | -1.14360 | 4.70930 | -3.11130 | H | 8.10380 | 2.62190 | 4.67640 |
| C | 2.18800 | 4.58160 | -3.88560 | H | 7.81640 | 4.29060 | 5.14330 |
| C | 3.45070 | 4.56140 | -1.65010 | H | 9.39350 | 3.80490 | 4.54820 |
| H | 3.42410 | 6.12870 | -3.14160 | H | 9.68820 | 2.88120 | 1.53100 |
| H | 1.78720 | 5.21440 | -4.67750 | H | 8.28460 | 1.83030 | 1.63900 |
| H | 1.39180 | 3.90790 | -3.56920 | H | 8.34510 | 3.09220 | 0.41850 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 3.77510 | 4.96810 | 1.84060 | H | 0.64000 | 9.71600 | -4.03910 |
| H | 4.95630 | 6.15380 | 2.28360 | H | -0.92920 | 10.15760 | -3.38410 |
| C | 3.29470 | 6.14060 | 3.58040 | C | -0.26700 | 7.97950 | -6.01110 |
| O | 3.51870 | 6.27090 | 4.78420 | H | 0.80190 | 7.85180 | -5.83200 |
| C | 2.10860 | 6.69930 | 2.91810 | H | -0.65360 | 7.02440 | -6.36770 |
| C | 1.74360 | 7.99580 | 2.97370 | H | -0.38200 | 8.70260 | -6.81890 |
| H | 1.51180 | 6.01710 | 2.33490 | C | 7.78940 | 6.81850 | 3.28460 |
| C | 2.42880 | 9.14190 | 3.70730 | H | 8.24680 | 6.59780 | 4.24960 |
| H | 0.86180 | 8.28660 | 2.42150 | H | 6.71200 | 6.76600 | 3.42320 |
| C | 2.90300 | 10.26800 | 2.74960 | H | 8.03620 | 7.85120 | 3.03740 |
| H | 3.29150 | 8.77380 | 4.25760 | C | 7.66220 | 6.21430 | 0.83390 |
| C | 1.46400 | 9.69260 | 4.76790 | H | 6.57650 | 6.13240 | 0.84730 |
| H | 1.91630 | 10.50660 | 5.33460 | H | 7.90940 | 7.23610 | 0.54510 |
| H | 1.18510 | 8.91500 | 5.47980 | H | 8.02230 | 5.55410 | 0.04410 |
| H | 0.54760 | 10.06880 | 4.31290 | C | 9.81300 | 5.93930 | 2.10080 |
| C | 4.20550 | 10.02760 | 1.92560 | H | 10.20640 | 5.28270 | 1.32410 |
| H | 3.12810 | 11.12960 | 3.38050 | H | 10.28890 | 5.65630 | 3.04040 |
| O | 1.81850 | 10.62860 | 1.91290 | H | 10.13680 | 6.95300 | 1.86260 |
| Si | 1.22650 | 12.19570 | 1.68950 | C | -0.15080 | 11.39440 | -0.63750 |
| C | -0.41570 | 12.05630 | 0.72500 | H | 0.26640 | 10.39490 | -0.51390 |
| C | 0.92860 | 13.00290 | 3.36980 | H | 0.55450 | 11.97100 | -1.23660 |
| C | 2.48580 | 13.19850 | 0.71010 | H | -1.06970 | 11.29680 | -1.21570 |
| H | 0.20980 | 12.43630 | 3.95940 | C | -1.39370 | 11.18690 | 1.53400 |
| H | 1.84560 | 13.07560 | 3.95200 | H | -0.97650 | 10.19590 | 1.72060 |
| H | 0.53270 | 14.01110 | 3.25840 | H | -2.33890 | 11.05270 | 1.00740 |
| H | 3.44680 | 13.24200 | 1.21980 | H | -1.61780 | 11.63270 | 2.50350 |
| H | 2.14580 | 14.22170 | 0.55820 | C | -1.00900 | 13.45980 | 0.51560 |
| H | 2.65240 | 12.76250 | -0.27320 | H | -1.94900 | 13.41510 | -0.03530 |
| C | 4.13050 | 8.98140 | 0.78090 | H | -0.32900 | 14.09940 | -0.04840 |
| C | 5.40010 | 9.72210 | 2.84610 | H | -1.21100 | 13.95380 | 1.46660 |
| H | 4.44640 | 10.98670 | 1.47240 | | | | |
| H | 5.47470 | 10.44800 | 3.65620 | ---------- | | | |
| H | 6.33960 | 9.75570 | 2.29370 | | | | |
| H | 5.32200 | 8.73110 | 3.29180 | Compound **5.4** | | | |
| C | 3.46330 | 9.45310 | -0.53480 | This structure was assigned as incorrect. | | | |
| H | 3.64310 | 8.08870 | 1.15410 | M06-2X/6-31g(d)//M06-L/6-31g(d) | | | |
| H | 5.13970 | 8.65150 | 0.53090 | SMD implicit solvation in ethanol was used. | | | |
| C | 4.33730 | 10.48420 | -1.27390 | | | | |
| H | 2.51570 | 9.93210 | -0.30190 | | | | |
| H | 4.53820 | 11.36860 | -0.67250 | Electronic Energy (M06-2X): -3279.54805176 hartree. | | | |
| H | 3.84780 | 10.83010 | -2.18490 | | | | |
| H | 5.29890 | 10.05650 | -1.55920 | Free Energy Correction (M06-L): 1.227698 hartree. | | | |
| C | -2.50030 | 8.56890 | -5.00380 | | | | |
| H | -2.93070 | 7.61910 | -5.32330 | | | | |
| H | -2.70250 | 9.30020 | -5.78690 | C | -1.28382 | -1.40818 | 1.92100 |
| H | -3.03820 | 8.88870 | -4.11050 | C | -2.72831 | -0.96326 | 2.09860 |
| C | -0.42210 | 9.79440 | -4.27780 | H | -0.65461 | -0.52489 | 1.72190 |
| H | -0.53220 | 10.55630 | -5.04960 | H | -1.22353 | -2.02598 | 1.01020 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -2.80580 | -0.15096 | 2.83590 | C | 2.30585 | 2.84946 | -1.87310 |
| H | -3.33683 | -1.79185 | 2.49380 | H | 1.49337 | 4.82007 | -2.46440 |
| C | -3.36171 | -0.50515 | 0.78720 | C | 3.57975 | 3.10314 | -2.67130 |
| O | -4.67700 | -0.00923 | 1.03390 | H | 1.97303 | 1.81327 | -2.04060 |
| H | -3.41432 | -1.38565 | 0.12090 | C | 2.58865 | 2.97366 | -0.35640 |
| C | -2.56759 | 0.59614 | 0.05910 | H | 4.37704 | 2.41273 | -2.36600 |
| Si | -6.09251 | -0.88831 | 0.81600 | H | 3.94347 | 4.12793 | -2.51870 |
| C | -6.08623 | -1.77451 | -0.83700 | H | 3.41095 | 2.96594 | -3.74600 |
| C | -6.29643 | -2.15211 | 2.18660 | C | 1.42424 | 2.46627 | 0.53030 |
| C | -7.45169 | 0.43431 | 0.88880 | O | 2.87217 | 4.33345 | -0.06660 |
| H | -5.59105 | -2.98692 | 2.07630 | H | 3.48104 | 2.35204 | -0.14790 |
| H | -7.30534 | -2.58759 | 2.18420 | Si | 4.12828 | 4.76323 | 0.98180 |
| H | -6.13283 | -1.71501 | 3.18000 | C | 5.74086 | 4.02221 | 0.37900 |
| H | -6.98384 | -2.40060 | -0.93470 | C | 4.15490 | 6.65703 | 0.89690 |
| H | -6.07552 | -1.08581 | -1.69190 | C | 3.75887 | 4.13344 | 2.70690 |
| H | -5.22384 | -2.44712 | -0.94100 | H | 4.56517 | 4.39013 | 3.40750 |
| C | -2.43017 | 1.84623 | 0.92100 | H | 2.82727 | 4.54665 | 3.11410 |
| C | -3.22179 | 0.90065 | -1.29440 | H | 3.66045 | 3.03914 | 2.72240 |
| H | -1.56110 | 0.19542 | -0.14550 | H | 5.67755 | 2.93221 | 0.26030 |
| H | -1.88347 | 1.62773 | 1.84790 | H | 6.54797 | 4.20960 | 1.10000 |
| H | -3.41306 | 2.25065 | 1.19880 | H | 6.06187 | 4.43810 | -0.58480 |
| H | -1.88006 | 2.63813 | 0.40020 | H | 0.47054 | 2.57879 | -0.00470 |
| H | -4.27948 | 1.15136 | -1.14830 | H | 1.37795 | 3.07998 | 1.43560 |
| C | -3.10510 | -0.21366 | -2.34920 | C | 1.63732 | 1.03107 | 0.94810 |
| O | -2.56087 | 2.06693 | -1.85270 | O | 2.01421 | 0.77356 | 2.09550 |
| H | -3.57382 | -1.10595 | -1.91290 | C | 1.42580 | 0.00747 | -0.09160 |
| C | -1.67251 | -0.50598 | -2.68730 | C | 1.99438 | -1.21334 | -0.15210 |
| C | -3.88480 | 0.16686 | -3.60800 | H | 0.78751 | 0.31698 | -0.92350 |
| H | -3.41898 | 1.01785 | -4.12270 | C | 2.98537 | -1.83555 | 0.78130 |
| H | -4.91809 | 0.44897 | -3.36600 | H | 1.76027 | -1.82003 | -1.03490 |
| H | -3.91781 | -0.66874 | -4.31700 | C | 2.57025 | -3.28154 | 1.15080 |
| C | -0.98122 | -1.63359 | -2.42930 | H | 3.02838 | -1.25645 | 1.70680 |
| H | -1.15029 | 0.29911 | -3.21190 | C | 4.36967 | -1.77857 | 0.13470 |
| H | 0.06417 | -1.67780 | -2.75050 | H | 5.12267 | -2.22838 | 0.79300 |
| C | -1.47174 | -2.81898 | -1.75680 | H | 4.66349 | -0.73718 | -0.05140 |
| C | -0.69976 | -3.88049 | -1.47200 | H | 4.39257 | -2.31227 | -0.82340 |
| H | -2.52574 | -2.84106 | -1.46600 | C | 1.09955 | -3.36522 | 1.59990 |
| H | -1.09427 | -4.76049 | -0.96620 | H | 3.22855 | -3.61355 | 1.97800 |
| H | 0.35904 | -3.89891 | -1.73690 | O | 2.75274 | -4.12815 | 0.01290 |
| C | -3.28325 | 3.17285 | -2.11890 | Si | 3.81932 | -5.43366 | -0.04140 |
| O | -4.49935 | 3.24756 | -1.97600 | C | 3.58331 | -6.13586 | -1.79020 |
| C | -2.47043 | 4.29473 | -2.58650 | C | 5.60433 | -4.92639 | 0.23850 |
| C | -1.12013 | 4.39781 | -2.66550 | C | 3.41820 | -6.71266 | 1.27050 |
| H | -3.06812 | 5.16704 | -2.84350 | H | 6.00244 | -4.25440 | -0.53140 |
| C | -0.09255 | 3.43260 | -2.36570 | H | 5.74563 | -4.43729 | 1.21130 |
| H | -0.74172 | 5.37481 | -2.97970 | H | 6.23841 | -5.82420 | 0.24910 |
| C | 1.20836 | 3.77968 | -2.27810 | H | 3.48190 | -6.28486 | 2.28010 |
| H | -0.37626 | 2.39870 | -2.17030 | H | 4.15398 | -7.52837 | 1.23220 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 2.42379 | -7.16164 | 1.16510 | H | 4.51358 | -7.65847 | -3.04220 |
| C | 0.81346 | -2.47462 | 2.81490 | H | 4.63058 | -8.00897 | -1.31220 |
| C | 0.65763 | -4.79761 | 1.86130 | H | 5.67180 | -6.77229 | -2.03960 |
| H | 0.51716 | -2.99251 | 0.74130 | --- | | | |
| H | 1.19832 | -5.23292 | 2.71460 | | | | |
| H | -0.41407 | -4.84000 | 2.09600 | Compound **5.4** | | | |
| H | 0.82802 | -5.44302 | 0.99200 | This structure was assigned as incorrect. | | | |
| C | -0.66453 | -2.16749 | 3.09660 | B3LYP/6-31g(d) | | | |
| H | 1.31438 | -1.50302 | 2.70100 | Gas phase. | | | |
| H | 1.26036 | -2.94492 | 3.70720 | | | | |
| C | -0.77322 | -1.36259 | 4.38690 | Electronic Energy: -3280.71956416 hartree. | | | |
| H | -1.21805 | -3.11308 | 3.23280 | | | | |
| H | -0.27810 | -0.38490 | 4.27660 | Free Energy: -3279.499792 hartree. | | | |
| H | -0.29143 | -1.88270 | 5.22530 | | | | |
| H | -1.81582 | -1.17388 | 4.67210 | C | -1.69173 | 1.38507 | -1.71570 |
| C | -7.11097 | 1.59591 | -0.05020 | C | -3.15370 | 0.92792 | -1.83753 |
| H | -6.99518 | 1.26980 | -1.09440 | H | -1.02448 | 0.51179 | -1.73057 |
| H | -6.18117 | 2.10129 | 0.24290 | H | -1.55423 | 1.85473 | -0.73238 |
| H | -7.91326 | 2.35092 | -0.03650 | H | -3.30140 | 0.31665 | -2.73358 |
| C | -8.78780 | -0.18047 | 0.45790 | H | -3.79612 | 1.80972 | -1.96218 |
| H | -9.07272 | -1.04326 | 1.07770 | C | -3.68076 | 0.14091 | -0.62135 |
| H | -8.76921 | -0.51697 | -0.58810 | O | -5.01973 | -0.29405 | -0.86758 |
| H | -9.59949 | 0.55924 | 0.54490 | H | -3.67004 | 0.82485 | 0.23984 |
| C | -7.58718 | 0.97121 | 2.31710 | C | -2.82734 | -1.10187 | -0.26002 |
| H | -7.88420 | 0.18542 | 3.02560 | Si | -6.48680 | 0.49049 | -0.64044 |
| H | -6.65018 | 1.41360 | 2.68440 | C | -6.56407 | 1.24898 | 1.09463 |
| H | -8.35707 | 1.75802 | 2.36370 | C | -6.71873 | 1.89011 | -1.89614 |
| C | 4.27681 | 7.11363 | -0.56010 | C | -7.80668 | -0.87327 | -0.88349 |
| H | 4.34053 | 8.21193 | -0.61720 | H | -6.00751 | 2.70643 | -1.72170 |
| H | 5.17711 | 6.71302 | -1.04790 | H | -7.72561 | 2.32013 | -1.82742 |
| H | 3.40961 | 6.80734 | -1.16060 | H | -6.57509 | 1.54042 | -2.92456 |
| C | 5.35741 | 7.18221 | 1.68820 | H | -7.51865 | 1.76643 | 1.25005 |
| H | 5.38003 | 8.28321 | 1.67100 | H | -6.46386 | 0.49609 | 1.88443 |
| H | 5.32671 | 6.87861 | 2.74450 | H | -5.77173 | 1.99429 | 1.23952 |
| H | 6.31221 | 6.83350 | 1.27040 | C | -2.72746 | -2.08650 | -1.43750 |
| C | 2.86881 | 7.23145 | 1.49880 | C | -3.37474 | -1.80746 | 1.00317 |
| H | 2.76281 | 6.97755 | 2.56260 | H | -1.82056 | -0.73558 | -0.02115 |
| H | 1.97091 | 6.86777 | 0.97980 | H | -2.30680 | -1.60186 | -2.32361 |
| H | 2.86403 | 8.33065 | 1.42700 | H | -3.71381 | -2.47938 | -1.70274 |
| C | 2.20440 | -6.79034 | -1.92040 | H | -2.07559 | -2.92722 | -1.18789 |
| H | 1.38611 | -6.08432 | -1.72100 | H | -4.40259 | -2.12174 | 0.82134 |
| H | 2.08498 | -7.63894 | -1.23230 | C | -3.33259 | -0.98376 | 2.31468 |
| H | 2.05449 | -7.17874 | -2.94060 | O | -2.58080 | -3.01009 | 1.21677 |
| C | 3.71672 | -5.02566 | -2.83790 | H | -3.93062 | -0.08592 | 2.12962 |
| H | 2.94384 | -4.25285 | -2.72560 | C | -1.93081 | -0.59164 | 2.71332 |
| H | 3.61832 | -5.43936 | -3.85440 | C | -4.01021 | -1.75964 | 3.46402 |
| H | 4.69433 | -4.52458 | -2.78850 | H | -3.43270 | -2.65045 | 3.73262 |
| C | 4.65849 | -7.19658 | -2.05270 | H | -5.01533 | -2.08724 | 3.17565 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -4.09082 | -1.12988 | 4.35603 | C | 2.14320 | 3.74346 | -1.18847 |
| C | -1.42595 | 0.64454 | 2.89046 | H | 2.70230 | 1.79907 | -1.96098 |
| H | -1.26910 | -1.43424 | 2.91131 | C | 4.44437 | 2.59207 | -1.04583 |
| H | -0.38498 | 0.72537 | 3.20656 | H | 4.77000 | 3.19323 | -1.90323 |
| C | -2.11341 | 1.91796 | 2.71588 | H | 4.93654 | 1.61748 | -1.10938 |
| C | -1.52466 | 3.11222 | 2.88645 | H | 4.77430 | 3.09223 | -0.13165 |
| H | -3.16601 | 1.89080 | 2.43943 | C | 0.60606 | 3.54139 | -1.31862 |
| H | -2.06808 | 4.04271 | 2.75378 | H | 2.50460 | 4.25681 | -2.09476 |
| H | -0.47793 | 3.19610 | 3.17136 | O | 2.42914 | 4.54064 | -0.03339 |
| C | -3.18230 | -4.21963 | 1.05055 | Si | 3.16053 | 6.04911 | 0.10932 |
| O | -4.37814 | -4.36235 | 0.87175 | C | 2.87021 | 6.53777 | 1.93921 |
| C | -2.24794 | -5.36506 | 1.06380 | C | 5.01267 | 5.98897 | -0.28011 |
| C | -0.90459 | -5.39116 | 1.22904 | C | 2.40431 | 7.31363 | -1.08058 |
| H | -2.76491 | -6.29876 | 0.86507 | H | 5.56268 | 5.29683 | 0.36581 |
| C | 0.00760 | -4.30674 | 1.54376 | H | 5.19435 | 5.68676 | -1.31804 |
| H | -0.43259 | -6.36897 | 1.12483 | H | 5.45418 | 6.98537 | -0.15288 |
| C | 1.34633 | -4.45545 | 1.54482 | H | 2.46222 | 6.96679 | -2.11970 |
| H | -0.42672 | -3.34425 | 1.78970 | H | 2.96193 | 8.25678 | -1.02708 |
| C | 2.32194 | -3.36624 | 1.89892 | H | 1.35401 | 7.53258 | -0.86447 |
| H | 1.78163 | -5.41769 | 1.27374 | C | 0.25387 | 2.77205 | -2.61365 |
| C | 3.30373 | -3.84395 | 2.98291 | C | -0.15298 | 4.87417 | -1.25469 |
| H | 1.75470 | -2.51324 | 2.29851 | H | 0.30122 | 2.94305 | -0.44932 |
| C | 3.08124 | -2.81950 | 0.65722 | H | 0.09038 | 5.50964 | -2.11624 |
| H | 4.00530 | -3.04523 | 3.25240 | H | -1.23521 | 4.71011 | -1.26265 |
| H | 3.88640 | -4.70007 | 2.62994 | H | 0.08791 | 5.42590 | -0.34420 |
| H | 2.76667 | -4.14496 | 3.88860 | C | -1.22463 | 2.36319 | -2.81511 |
| C | 2.11372 | -2.13987 | -0.36661 | H | 0.84859 | 1.85301 | -2.68021 |
| O | 3.81405 | -3.87838 | 0.06472 | H | 0.55959 | 3.39277 | -3.46994 |
| H | 3.78477 | -2.06252 | 1.03854 | C | -1.39091 | 1.76757 | -4.22356 |
| Si | 5.17152 | -3.79337 | -0.94073 | H | -1.85613 | 3.26159 | -2.76169 |
| C | 6.28561 | -2.36801 | -0.38708 | H | -0.81315 | 0.83963 | -4.32815 |
| C | 6.03778 | -5.48993 | -0.73134 | H | -1.03310 | 2.46729 | -4.98803 |
| C | 4.64359 | -3.51464 | -2.72996 | H | -2.43673 | 1.53815 | -4.45183 |
| H | 5.51254 | -3.49198 | -3.39913 | C | -7.61548 | -2.00393 | 0.15079 |
| H | 3.97153 | -4.30514 | -3.08415 | H | -7.69762 | -1.63593 | 1.18146 |
| H | 4.12275 | -2.55558 | -2.82827 | H | -6.64598 | -2.50227 | 0.04646 |
| H | 5.81295 | -1.39835 | -0.58222 | H | -8.39245 | -2.77134 | 0.02037 |
| H | 7.23004 | -2.38196 | -0.94468 | C | -9.21865 | -0.27089 | -0.71032 |
| H | 6.53151 | -2.41830 | 0.67994 | H | -9.42289 | 0.52458 | -1.43757 |
| H | 1.10222 | -2.09701 | 0.05403 | H | -9.36960 | 0.14530 | 0.29365 |
| H | 2.07033 | -2.74677 | -1.27243 | H | -9.98277 | -1.04777 | -0.85643 |
| C | 2.55779 | -0.72969 | -0.73522 | C | -7.68180 | -1.46898 | -2.30274 |
| O | 3.09432 | -0.49132 | -1.81552 | H | -7.85623 | -0.71562 | -3.08106 |
| C | 2.32697 | 0.30804 | 0.29937 | H | -6.68994 | -1.90277 | -2.47007 |
| C | 2.47689 | 1.63888 | 0.14816 | H | -8.42436 | -2.26696 | -2.44835 |
| H | 1.97279 | -0.05864 | 1.26191 | C | 6.56630 | -5.65520 | 0.70881 |
| C | 2.91436 | 2.39947 | -1.07527 | H | 7.05978 | -6.63122 | 0.82603 |
| H | 2.26566 | 2.26415 | 1.01545 | H | 7.30352 | -4.88499 | 0.96638 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 5.75771 | -5.60464 | 1.44680 | H | -6.05010 | 1.31160 | -2.78020 |
| C | 7.22688 | -5.58822 | -1.71284 | H | -7.71000 | 0.75280 | -2.55090 |
| H | 7.73729 | -6.55524 | -1.59627 | H | -6.58180 | -0.19550 | -3.52820 |
| H | 6.90552 | -5.51428 | -2.75858 | H | -7.56090 | 0.63910 | 0.56630 |
| H | 7.97535 | -4.80530 | -1.53575 | H | -6.17030 | -0.08950 | 1.37010 |
| C | 5.04137 | -6.62974 | -1.03388 | H | -5.98720 | 1.43160 | 0.47770 |
| H | 4.65593 | -6.57604 | -2.05939 | C | -1.76810 | -1.94220 | -1.53730 |
| H | 4.18305 | -6.60590 | -0.35330 | C | -2.90560 | -2.46040 | 0.65340 |
| H | 5.53205 | -7.60762 | -0.92022 | H | -1.55320 | -0.84550 | 0.29780 |
| C | 1.35936 | 6.55866 | 2.25526 | H | -1.36220 | -1.15070 | -2.17920 |
| H | 0.90243 | 5.57512 | 2.09854 | H | -2.52980 | -2.48510 | -2.11320 |
| H | 0.81889 | 7.28332 | 1.63345 | H | -0.94840 | -2.63970 | -1.32710 |
| H | 1.19226 | 6.84288 | 3.30461 | H | -3.72650 | -2.98240 | 0.14900 |
| C | 3.55822 | 5.51996 | 2.87437 | C | -3.39380 | -2.00360 | 2.03760 |
| H | 3.16705 | 4.50708 | 2.72525 | O | -1.83170 | -3.42420 | 0.84570 |
| H | 3.38838 | 5.79102 | 3.92673 | H | -4.27620 | -1.37390 | 1.84740 |
| H | 4.64338 | 5.48656 | 2.71894 | C | -2.35060 | -1.22100 | 2.78060 |
| C | 3.45777 | 7.94171 | 2.20332 | C | -3.84810 | -3.20690 | 2.86590 |
| H | 3.29811 | 8.23031 | 3.25227 | H | -2.99560 | -3.83250 | 3.15970 |
| H | 2.98421 | 8.71049 | 1.58037 | H | -4.54440 | -3.83800 | 2.29770 |
| H | 4.53845 | 7.97934 | 2.01878 | H | -4.35360 | -2.88080 | 3.78240 |
| ---------- | | | | C | -2.40430 | 0.06700 | 3.17620 |
| | | | | H | -1.44870 | -1.78760 | 3.03260 |
| Compound **5.4** | | | | H | -1.54330 | 0.47000 | 3.71780 |
| This structure was assigned as ambiguous. | | | | C | -3.48180 | 1.00540 | 2.93670 |
| M06-2X/6-31g(d)//M06-L/6-31g(d) | | | | C | -3.43510 | 2.30800 | 3.26050 |
| SMD implicit solvation in ethanol was used. | | | | H | -4.38350 | 0.62430 | 2.45140 |
| | | | | H | -4.26810 | 2.97710 | 3.04930 |
| | | | | H | -2.56880 | 2.74640 | 3.75930 |
| Electronic Energy (M06-2X): -3279.54590750 hartree. | | | | C | -2.00810 | -4.66810 | 0.34950 |
| | | | | O | -3.07610 | -5.07780 | -0.09390 |
| Free Energy Correction (M06-L): 1.230005 hartree. | | | | C | -0.80120 | -5.49050 | 0.35820 |
| | | | | C | 0.48740 | -5.13530 | 0.58730 |
| | | | | H | -0.99910 | -6.51620 | 0.05240 |
| C | -3.52860 | 2.20860 | -1.04800 | C | 1.06890 | -3.87670 | 0.98240 |
| C | -2.84060 | 0.87840 | -1.33810 | H | 1.22080 | -5.93320 | 0.43960 |
| H | -3.55360 | 2.35520 | 0.04510 | C | 2.40880 | -3.72410 | 1.03780 |
| H | -4.58350 | 2.16230 | -1.36080 | H | 0.41740 | -3.04350 | 1.24690 |
| H | -1.77120 | 0.95910 | -1.08780 | C | 3.13870 | -2.49580 | 1.47320 |
| H | -2.88460 | 0.63520 | -2.41040 | H | 3.03950 | -4.57700 | 0.76600 |
| C | -3.41680 | -0.29350 | -0.54180 | C | 4.09060 | -2.84190 | 2.61800 |
| O | -4.50770 | -0.91440 | -1.21840 | H | 2.40930 | -1.74900 | 1.82530 |
| H | -3.77190 | 0.10390 | 0.42420 | C | 3.92010 | -1.85000 | 0.30800 |
| C | -2.35410 | -1.36260 | -0.25450 | H | 4.64710 | -1.95460 | 2.94650 |
| Si | -6.14010 | -0.53230 | -1.09190 | H | 4.81720 | -3.60370 | 2.30590 |
| C | -6.48260 | 0.45160 | 0.46640 | H | 3.54430 | -3.23620 | 3.48280 |
| C | -6.66680 | 0.41680 | -2.62060 | C | 3.00870 | -1.27240 | -0.79170 |
| C | -7.04150 | -2.20620 | -1.02850 | O | 4.78810 | -2.81910 | -0.25690 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | 4.50550 | -1.01280 | 0.73380 | C | -3.09350 | 3.43780 | -3.21790 |
| Si | 6.40840 | -2.45410 | -0.57730 | H | -3.36970 | 4.32300 | -1.29790 |
| C | 7.29460 | -1.99680 | 1.00870 | H | -2.60940 | 2.57760 | -3.70120 |
| C | 7.08030 | -4.06320 | -1.31920 | H | -2.67590 | 4.34370 | -3.67740 |
| C | 6.51260 | -1.00910 | -1.76670 | H | -4.16150 | 3.40190 | -3.47160 |
| H | 7.55700 | -0.73050 | -1.96270 | C | -6.45230 | -3.16620 | -2.06650 |
| H | 6.04340 | -1.22009 | -2.73610 | H | -5.40700 | -3.41950 | -1.83960 |
| H | 6.02010 | -0.11600 | -1.35580 | H | -6.48080 | -2.75190 | -3.08460 |
| H | 6.86170 | -1.10319 | 1.47840 | H | -7.01930 | -4.11080 | -2.08700 |
| H | 8.34850 | -1.76160 | 0.80640 | C | -6.89400 | -2.83540 | 0.36010 |
| H | 7.27730 | -2.80009 | 1.75610 | H | -7.33710 | -2.21300 | 1.15040 |
| H | 2.23720 | -2.01010 | -1.05410 | H | -5.83930 | -3.00440 | 0.62200 |
| H | 3.62760 | -1.08640 | -1.67660 | H | -7.39560 | -3.81560 | 0.39870 |
| C | 2.40230 | 0.04330 | -0.35930 | C | -8.53150 | -2.00010 | -1.32410 |
| O | 3.03270 | 1.09250 | -0.52880 | H | -9.00020 | -1.28400 | -0.63300 |
| C | 1.09600 | -0.01990 | 0.30510 | H | -8.70500 | -1.63520 | -2.34580 |
| C | 0.52130 | 0.95040 | 1.04730 | H | -9.07970 | -2.95020 | -1.22170 |
| H | 0.58760 | -0.98440 | 0.24120 | C | 6.33980 | -4.39459 | -2.61850 |
| C | 1.01750 | 2.32960 | 1.34160 | H | 6.70150 | -5.34659 | -3.03830 |
| H | -0.43920 | 0.69470 | 1.51010 | H | 5.25750 | -4.49910 | -2.46080 |
| C | 0.55290 | 3.29510 | 0.21370 | H | 6.48980 | -3.62500 | -3.38840 |
| H | 2.11370 | 2.32470 | 1.28560 | C | 6.88630 | -5.21289 | -0.32520 |
| C | 0.58570 | 2.77640 | 2.73200 | H | 7.29600 | -6.15079 | -0.73270 |
| H | 0.87530 | 3.81850 | 2.91850 | H | 7.39660 | -5.02679 | 0.63060 |
| H | 1.05190 | 2.15530 | 3.50710 | H | 5.82490 | -5.39199 | -0.10410 |
| H | -0.50280 | 2.69620 | 2.85820 | C | 8.57460 | -3.90449 | -1.61840 |
| C | -0.98300 | 3.41650 | 0.07920 | H | 9.16030 | -3.70300 | -0.71050 |
| H | 0.94050 | 2.85880 | -0.72530 | H | 8.77170 | -3.08880 | -2.32850 |
| O | 1.11250 | 4.58390 | 0.40180 | H | 8.97960 | -4.82580 | -2.06600 |
| Si | 2.63680 | 5.06820 | -0.13060 | C | 2.00510 | 7.33170 | 1.42930 |
| C | 2.55920 | 6.95800 | 0.05000 | H | 2.61440 | 6.91820 | 2.24630 |
| C | 4.00310 | 4.35450 | 0.93870 | H | 0.97730 | 6.97100 | 1.57110 |
| C | 2.88650 | 4.55120 | -1.91470 | H | 1.99060 | 8.42560 | 1.56000 |
| H | 3.83420 | 4.53390 | 2.00890 | C | 3.96230 | 7.55470 | -0.10160 |
| H | 4.11730 | 3.27210 | 0.79900 | H | 4.63100 | 7.24530 | 0.71330 |
| H | 4.97060 | 4.80760 | 0.68170 | H | 3.91950 | 8.65530 | -0.08480 |
| H | 3.08590 | 3.47590 | -2.00970 | H | 4.44080 | 7.26660 | -1.04920 |
| H | 3.74500 | 5.07390 | -2.35840 | C | 1.64950 | 7.54600 | -1.03340 |
| H | 2.01160 | 4.77860 | -2.53780 | H | 1.55330 | 8.63660 | -0.91030 |
| C | -1.37350 | 3.52660 | -1.39940 | H | 0.63390 | 7.12590 | -0.99710 |
| C | -1.58510 | 4.56440 | 0.88420 | H | 2.04560 | 7.36910 | -2.04310 |
| H | -1.40470 | 2.47700 | 0.47510 | ---------- | | | |
| H | -1.33380 | 5.53520 | 0.43820 | | | | |
| H | -2.68040 | 4.48700 | 0.90110 | Compound **5.4** | | | |
| H | -1.24120 | 4.58350 | 1.92470 | This structure was assigned as ambiguous. | | | |
| C | -2.87250 | 3.42950 | -1.70940 | B3LYP/6-31g(d) | | | |
| H | -0.84710 | 2.73990 | -1.96430 | Gas phase. | | | |
| H | -0.98810 | 4.48140 | -1.79630 | | | | |

Electronic Energy: -3280.71780164 hartree.
Free Energy: -3279.499294 hartree.

| | | | |
|---|---|---|---|
| C | -3.45116 | 2.48847 | -0.42375 |
| C | -2.94129 | 1.15754 | -0.99992 |
| H | -3.29035 | 2.48091 | 0.66334 |
| H | -4.53827 | 2.55830 | -0.56136 |
| H | -1.85455 | 1.11325 | -0.86197 |
| H | -3.11994 | 1.10347 | -2.07921 |
| C | -3.56872 | -0.09977 | -0.34683 |
| O | -4.66230 | -0.61021 | -1.11190 |
| H | -3.93155 | 0.18628 | 0.64984 |
| C | -2.51780 | -1.22752 | -0.18032 |
| Si | -6.31208 | -0.30100 | -1.09206 |
| C | -6.89427 | 0.02846 | 0.68067 |
| C | -6.72522 | 1.20730 | -2.15972 |
| C | -7.13499 | -1.86328 | -1.83619 |
| H | -6.34617 | 2.13519 | -1.71785 |
| H | -7.80945 | 1.32372 | -2.27807 |
| H | -6.28941 | 1.11671 | -3.16107 |
| H | -7.97062 | 0.23752 | 0.70319 |
| H | -6.71144 | -0.82497 | 1.34384 |
| H | -6.38957 | 0.90239 | 1.11088 |
| C | -2.01468 | -1.72323 | -1.54685 |
| C | -3.03667 | -2.40082 | 0.67694 |
| H | -1.67615 | -0.77480 | 0.36061 |
| H | -1.63529 | -0.89267 | -2.15037 |
| H | -2.82330 | -2.20215 | -2.10721 |
| H | -1.20228 | -2.44496 | -1.42874 |
| H | -3.89852 | -2.85714 | 0.18923 |
| C | -3.42399 | -2.05966 | 2.13767 |
| O | -1.97664 | -3.40220 | 0.71873 |
| H | -4.22456 | -1.31556 | 2.07476 |
| C | -2.27027 | -1.50261 | 2.93470 |
| C | -4.00573 | -3.29771 | 2.85451 |
| H | -3.23802 | -4.06327 | 3.00829 |
| H | -4.81343 | -3.74685 | 2.26670 |
| H | -4.39983 | -3.01761 | 3.83681 |
| C | -2.20508 | -0.33390 | 3.60296 |
| H | -1.40902 | -2.16670 | 3.00237 |
| H | -1.29201 | -0.12159 | 4.16098 |
| C | -3.22735 | 0.70312 | 3.68154 |
| C | -3.06541 | 1.85832 | 4.34615 |
| H | -4.17385 | 0.52209 | 3.17536 |
| H | -3.84826 | 2.60940 | 4.38725 |
| H | -2.14386 | 2.08546 | 4.87844 |
| C | -2.24651 | -4.64227 | 0.22717 |
| O | -3.35108 | -4.99616 | -0.14372 |
| C | -1.07361 | -5.53687 | 0.15084 |
| C | 0.23035 | -5.30569 | 0.43045 |
| H | -1.35037 | -6.51073 | -0.24108 |
| C | 0.88367 | -4.12343 | 0.96505 |
| H | 0.90740 | -6.13513 | 0.22162 |
| C | 2.22601 | -4.03437 | 1.05046 |
| H | 0.25569 | -3.30345 | 1.29759 |
| C | 2.99599 | -2.86547 | 1.60401 |
| H | 2.83307 | -4.86651 | 0.69332 |
| C | 3.92917 | -3.32877 | 2.73878 |
| H | 2.28593 | -2.13792 | 2.01822 |
| C | 3.79730 | -2.12248 | 0.49740 |
| H | 3.35670 | -3.79842 | 3.54546 |
| H | 4.47850 | -2.47917 | 3.16138 |
| H | 4.65952 | -4.05643 | 2.37060 |
| C | 2.88234 | -1.39712 | -0.52931 |
| O | 4.63517 | -3.05799 | -0.16881 |
| H | 4.41364 | -1.35993 | 0.99895 |
| Si | 6.20182 | -2.74843 | -0.72397 |
| C | 7.30480 | -2.26529 | 0.73517 |
| C | 6.75058 | -4.39938 | -1.51533 |
| C | 6.19952 | -1.32595 | -1.96971 |
| H | 7.22221 | -1.07332 | -2.27580 |
| H | 5.63384 | -1.57103 | -2.87601 |
| H | 5.75413 | -0.42108 | -1.53839 |
| H | 6.96704 | -1.33105 | 1.20012 |
| H | 8.33864 | -2.10316 | 0.40669 |
| H | 7.31799 | -3.03680 | 1.51298 |
| H | 2.01641 | -2.02814 | -0.75777 |
| H | 3.45524 | -1.25028 | -1.44643 |
| C | 2.46154 | -0.01309 | -0.04429 |
| O | 3.16073 | 0.96135 | -0.31928 |
| C | 1.23809 | 0.06926 | 0.78569 |
| C | 0.82303 | 1.13136 | 1.50891 |
| H | 0.64976 | -0.84339 | 0.84256 |
| C | 1.43539 | 2.50201 | 1.60120 |
| H | -0.08493 | 0.98171 | 2.09554 |
| C | 0.84717 | 3.41497 | 0.46713 |
| H | 2.49580 | 2.41437 | 1.35313 |
| C | 1.30415 | 3.06827 | 3.02323 |
| H | 1.64174 | 4.10824 | 3.05223 |
| H | 1.92042 | 2.49094 | 3.72234 |
| H | 0.27079 | 3.03028 | 3.38702 |
| C | -0.68866 | 3.65950 | 0.53365 |
| H | 1.05061 | 2.86462 | -0.46095 |
| O | 1.53532 | 4.65863 | 0.43689 |
| Si | 2.90702 | 5.05941 | -0.46031 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C | 2.91977 | 6.97572 | -0.45433 | H | 0.74319 | 7.17461 | -0.68403 |
| C | 4.46867 | 4.36449 | 0.34812 | H | 1.62502 | 7.20449 | -2.22100 |
| C | 2.76798 | 4.35161 | -2.20786 | H | 1.65803 | 8.61667 | -1.15627 |
| H | 4.55009 | 4.65196 | 1.40276 | C | 2.92783 | 7.49183 | 1.00086 |
| H | 4.47005 | 3.27020 | 0.29106 | H | 2.04978 | 7.14330 | 1.55564 |
| H | 5.37083 | 4.72063 | -0.16474 | H | 2.92145 | 8.59181 | 1.01817 |
| H | 2.82289 | 3.25689 | -2.18611 | H | 3.82100 | 7.16316 | 1.54661 |
| H | 3.59444 | 4.70481 | -2.83681 | C | 4.17588 | 7.50007 | -1.18347 |
| H | 1.83028 | 4.63579 | -2.69873 | H | 4.18273 | 8.59983 | -1.18902 |
| C | -1.27032 | 3.81044 | -0.89158 | H | 4.21322 | 7.17198 | -2.22992 |
| C | -1.08519 | 4.85269 | 1.41932 | H | 5.10261 | 7.17291 | -0.69678 |
| H | -1.12396 | 2.75258 | 0.97394 | ---------- | | | |
| H | -0.74275 | 5.79258 | 0.97613 | | | | |
| H | -2.17380 | 4.90501 | 1.52954 | Compound **5.4** | | | |
| H | -0.65693 | 4.78810 | 2.42183 | This structure was assigned as ambiguous. | | | |
| C | -2.81036 | 3.76704 | -1.01980 | B3LYP/6-31g(d) | | | |
| H | -0.84772 | 3.02488 | -1.53323 | SMD implicit solvation in ethanol was | | | |
| H | -0.91539 | 4.76128 | -1.31415 | used. | | | |
| C | -3.22034 | 3.98349 | -2.48662 | | | | |
| H | -3.22247 | 4.61077 | -0.44817 | Electronic Energy: -3280.76246456 har- | | | |
| H | -2.81723 | 3.20156 | -3.14159 | tree. | | | |
| H | -2.84775 | 4.94516 | -2.85888 | Free Energy: -3279.544487 hartree. | | | |
| H | -4.31123 | 3.98177 | -2.59947 | | | | |
| C | -8.66769 | -1.67077 | -1.87985 | C | -2.65913 | 0.99949 | 1.81801 |
| H | -8.96273 | -0.81329 | -2.49677 | C | -3.49463 | 0.71426 | 0.55851 |
| H | -9.09408 | -1.52689 | -0.87912 | H | -1.65762 | 0.56743 | 1.70466 |
| H | -9.14880 | -2.56038 | -2.31106 | H | -3.11576 | 0.47397 | 2.66957 |
| C | -6.61423 | -2.08880 | -3.27227 | H | -3.02386 | 1.15105 | -0.33000 |
| H | -7.06609 | -2.99321 | -3.70515 | H | -4.47208 | 1.19911 | 0.65631 |
| H | -5.52663 | -2.22017 | -3.28976 | C | -3.76568 | -0.78390 | 0.31539 |
| H | -6.86306 | -1.25100 | -3.93530 | O | -4.70523 | -0.94801 | -0.76246 |
| C | -6.81794 | -3.11419 | -0.98945 | H | -4.20609 | -1.18466 | 1.23719 |
| H | -5.74818 | -3.34688 | -0.97833 | C | -2.49279 | -1.60430 | -0.01946 |
| H | -7.15303 | -3.00450 | 0.04997 | Si | -6.39049 | -1.00435 | -0.67852 |
| H | -7.33469 | -3.99230 | -1.40329 | C | -6.94466 | -2.21057 | 0.66461 |
| C | 8.16904 | -4.24941 | -2.10823 | C | -7.11071 | 0.69748 | -0.27894 |
| H | 8.49468 | -5.19727 | -2.56025 | C | -6.93099 | -1.59326 | -2.42089 |
| H | 8.20807 | -3.48523 | -2.89425 | H | -6.82194 | 1.02532 | 0.72750 |
| H | 8.91106 | -3.98355 | -1.34489 | H | -8.20827 | 0.67536 | -0.30401 |
| C | 5.77128 | -4.79513 | -2.64181 | H | -6.78019 | 1.46738 | -0.98659 |
| H | 6.07150 | -5.75422 | -3.08835 | H | -8.03862 | -2.30288 | 0.66897 |
| H | 4.74830 | -4.90670 | -2.26605 | H | -6.53022 | -3.21618 | 0.52812 |
| H | 5.75336 | -4.05278 | -3.44916 | H | -6.65392 | -1.86033 | 1.66321 |
| C | 6.76393 | -5.51760 | -0.45064 | C | -1.90500 | -1.22110 | -1.38879 |
| H | 5.77408 | -5.66041 | -0.00222 | C | -2.75214 | -3.12563 | 0.05758 |
| H | 7.47253 | -5.30644 | 0.35972 | H | -1.75240 | -1.36469 | 0.75353 |
| H | 7.06411 | -6.47326 | -0.90468 | H | -1.77063 | -0.13842 | -1.47349 |
| C | 1.66383 | 7.51666 | -1.17004 | H | -2.55935 | -1.54076 | -2.20690 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H | -0.92457 | -1.67926 | -1.54155 | H | 3.47797 | -1.64893 | -1.83717 |
| H | -3.50975 | -3.40941 | -0.67464 | H | 4.71416 | -0.39164 | -1.60740 |
| C | -3.16353 | -3.68556 | 1.44178 | C | 2.74084 | 0.16253 | -0.97890 |
| O | -1.50389 | -3.78920 | -0.32028 | O | 1.56326 | -0.13223 | -1.20389 |
| H | -4.11547 | -3.20993 | 1.69467 | C | 3.18256 | 1.50207 | -0.53423 |
| C | -2.13974 | -3.38641 | 2.51045 | C | 2.50693 | 2.66584 | -0.64121 |
| C | -3.42247 | -5.20574 | 1.36431 | H | 4.19116 | 1.53831 | -0.12624 |
| H | -2.49896 | -5.76406 | 1.17351 | C | 1.18521 | 2.93644 | -1.30453 |
| H | -4.13486 | -5.44269 | 0.56498 | H | 3.02344 | 3.55760 | -0.28500 |
| H | -3.83909 | -5.56648 | 2.31107 | C | 0.18864 | 3.74638 | -0.42323 |
| C | -2.34944 | -2.85315 | 3.73054 | H | 0.69185 | 1.98966 | -1.53139 |
| H | -1.11939 | -3.67642 | 2.26120 | C | 1.46463 | 3.65606 | -2.64256 |
| H | -1.48522 | -2.73132 | 4.38507 | H | 0.52340 | 3.87876 | -3.15872 |
| C | -3.62143 | -2.41555 | 4.29500 | H | 2.00790 | 4.59490 | -2.49603 |
| C | -3.74361 | -1.87270 | 5.51767 | H | 2.06754 | 3.01962 | -3.30020 |
| H | -4.51693 | -2.54463 | 3.68920 | C | -0.33181 | 2.93962 | 0.80313 |
| H | -4.70857 | -1.55924 | 5.90774 | H | -0.67363 | 3.94100 | -1.07690 |
| H | -2.88181 | -1.72625 | 6.16705 | O | 0.77489 | 4.99405 | -0.02847 |
| C | -1.48874 | -4.63452 | -1.37083 | Si | 0.26413 | 6.57580 | -0.32840 |
| O | -2.48488 | -4.92058 | -2.02817 | C | 1.81945 | 7.65194 | -0.01243 |
| C | -0.16985 | -5.22180 | -1.66164 | C | -0.38164 | 6.77582 | -2.09235 |
| C | 1.05862 | -4.84929 | -1.22459 | C | -1.13130 | 7.07430 | 0.84538 |
| H | -0.23731 | -6.04946 | -2.36191 | H | 0.39586 | 6.66216 | -2.85582 |
| C | 1.44319 | -3.74611 | -0.36649 | H | -1.17666 | 6.05210 | -2.31274 |
| H | 1.89127 | -5.44700 | -1.59723 | H | -0.82182 | 7.77455 | -2.21296 |
| C | 2.73091 | -3.51300 | -0.04114 | H | -2.05979 | 6.54087 | 0.60788 |
| H | 0.66886 | -3.08397 | 0.00507 | H | -1.34606 | 8.14720 | 0.75193 |
| C | 3.19704 | -2.38583 | 0.83917 | H | -0.89253 | 6.87671 | 1.89702 |
| H | 3.50334 | -4.18641 | -0.41431 | C | -1.77924 | 3.35063 | 1.15626 |
| C | 3.66074 | -2.92883 | 2.20544 | C | 0.59335 | 3.02721 | 2.02682 |
| H | 2.35216 | -1.70857 | 1.01631 | H | -0.34864 | 1.89234 | 0.47316 |
| C | 4.30874 | -1.54003 | 0.16531 | H | 0.56236 | 4.02369 | 2.48150 |
| H | 4.02635 | -2.11392 | 2.84211 | H | 0.29071 | 2.30435 | 2.79244 |
| H | 4.46344 | -3.66525 | 2.09598 | H | 1.63495 | 2.80803 | 1.77170 |
| H | 2.82821 | -3.41608 | 2.72485 | C | -2.51191 | 2.48976 | 2.20967 |
| C | 3.84185 | -0.87530 | -1.15446 | H | -2.37821 | 3.36250 | 0.23439 |
| O | 5.43482 | -2.37272 | -0.12166 | H | -1.76741 | 4.38660 | 1.52083 |
| H | 4.59340 | -0.75354 | 0.87824 | C | -3.86309 | 3.13213 | 2.56425 |
| Si | 7.06195 | -1.97879 | 0.14479 | H | -1.90976 | 2.49876 | 3.12903 |
| C | 7.36024 | -1.69935 | 1.98802 | H | -4.50755 | 3.24774 | 1.68397 |
| C | 8.02609 | -3.48687 | -0.52910 | H | -3.71923 | 4.13089 | 2.99538 |
| C | 7.51962 | -0.39525 | -0.77680 | H | -4.41037 | 2.52932 | 3.30046 |
| H | 8.57593 | -0.14555 | -0.61136 | C | -6.37755 | -0.64127 | -3.50165 |
| H | 7.36361 | -0.47472 | -1.85889 | H | -5.28154 | -0.61112 | -3.49867 |
| H | 6.93168 | 0.45856 | -0.41638 | H | -6.73953 | 0.38648 | -3.36971 |
| H | 6.76455 | -0.85609 | 2.36090 | H | -6.69401 | -0.97087 | -4.50293 |
| H | 8.41310 | -1.45313 | 2.17832 | C | -6.40466 | -3.01944 | -2.68805 |
| H | 7.10941 | -2.57680 | 2.59506 | H | -6.79851 | -3.74506 | -1.96497 |

| | | | |
|---|---|---|---|
| H | -5.30969 | -3.07181 | -2.64892 |
| H | -6.71121 | -3.36073 | -3.68863 |
| C | -8.47253 | -1.60725 | -2.50723 |
| H | -8.92365 | -2.27560 | -1.76256 |
| H | -8.90402 | -0.60889 | -2.36428 |
| H | -8.79669 | -1.96098 | -3.49752 |
| C | 9.54248 | -3.23912 | -0.37311 |
| H | 10.10963 | -4.09897 | -0.75973 |
| H | 9.87729 | -2.35458 | -0.92949 |
| H | 9.83531 | -3.10398 | 0.67598 |
| C | 7.70306 | -3.69554 | -2.02376 |
| H | 8.26171 | -4.55726 | -2.41904 |
| H | 6.63675 | -3.89289 | -2.18840 |
| H | 7.97780 | -2.82407 | -2.63164 |
| C | 7.64539 | -4.76419 | 0.24869 |
| H | 6.57583 | -4.99223 | 0.16587 |
| H | 7.88867 | -4.68523 | 1.31588 |
| H | 8.19590 | -5.63126 | -0.14630 |
| C | 2.26033 | 7.53034 | 1.46185 |
| H | 2.51453 | 6.49720 | 1.72939 |
| H | 1.48194 | 7.87161 | 2.15573 |
| H | 3.15349 | 8.14615 | 1.64712 |
| C | 2.98718 | 7.20936 | -0.91838 |
| H | 3.29322 | 6.17635 | -0.71605 |
| H | 3.86636 | 7.84961 | -0.74924 |
| H | 2.73550 | 7.28219 | -1.98395 |
| C | 1.48913 | 9.12973 | -0.31658 |
| H | 2.36472 | 9.76491 | -0.11445 |
| H | 0.66629 | 9.50890 | 0.30232 |
| H | 1.21411 | 9.28422 | -1.36789 |

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